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MICROMINERALOGICAL AND TEXTURAL FEATURES IN RELATION TO THE GENESIS OF BAUXITE OF ISZKASZENTGYÖRGY

S. ANTAL

INTRODUCTION

The task of the present paper is to study within profiles of a single bauxite body the genetically evaluable relations between the quantity of the accessory detrital minerals and the textural features of the bauxite.

The samples selected for this study comprise the total bauxite profile of six productive boreholes of the Rákhegy bauxite body, Iszkaszentgyörgy (Bakony Mountains, Hungary). The boreholes are arranged in dip and strike direction of the bauxite deposit. The samples are as follows (enumerated downwards):

Borehole Rp—19: Samples Nos. 1 to 13
Rp—40: Samples Nos. 14 to 19
Rp—30: Sample No. 20
Rp—17: Samples Nos. 21 to 32
Rp—26: Samples Nos. 33 to 39
Rp—23: Samples Nos. 40 to 46

The geology of the area is as shown on *Fig. 1.*

The bauxite body of Rákhegy is bordered from the József deposit to the south by a tectonic fault, from here it is extended to NNE, in 2,5 km length; its average width is 400 m, the average dip is 0/10°, the thickness average is 5,9 m. The deposit lies on the karstic surface of the Carnian "Hauptdolomit", usually with an intervening dusting dolomitic zone. The bauxite body is paraconformably overlain by the transgressive Upper Lutetian coal-bearing sequence.

MICROMINERALOGICAL STUDIES

In order to find out quantitative distribution of the accessory detrital minerals along profile, the 0,2—0,1 mm diametre range of 45 bauxite samples have been treated. On the basis of the random samples derived from the other grain-size intervals, the mineral percentage composition of these latter is nearly the same as that of the 0,2—0,1 mm diametre range. The exception is the coarsest (0,63—0,32 mm) fraction, but its quantity is negligible when compared to the total amount of the settling rest.

The partly optically, partly X-ray analitically recognizable minerals are shown in *Fig. 2.* These minerals with their probable origin is summarized in Table I. In addition to the previously known minerals [KOMLÓSSY, 1969] the following new minerals could have been proved: lithiophorite, zircon, spessartine, staurolite, glauconite and spinel.

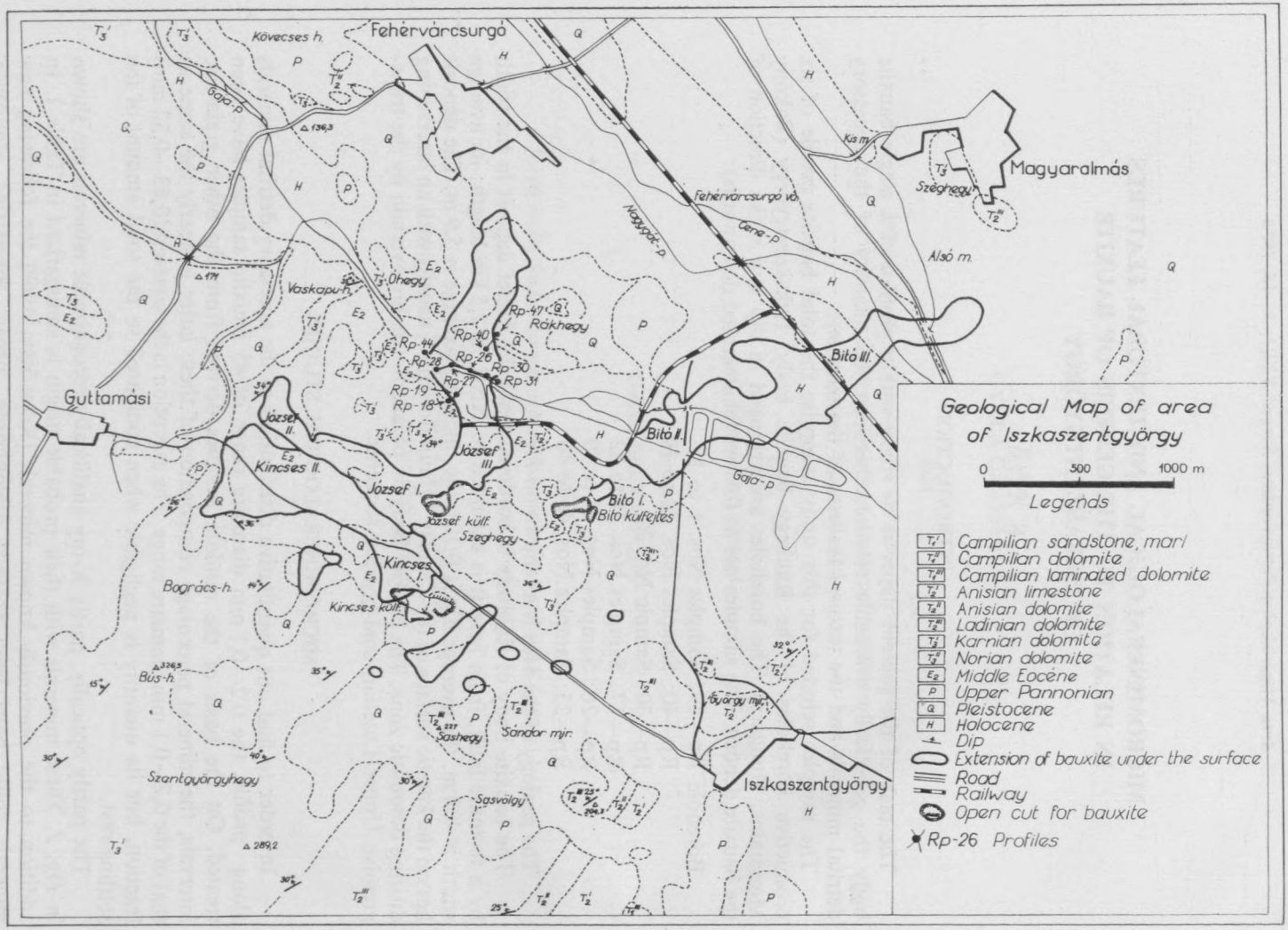

Fig. 1. Geological map of the bauxite area of Iszkaszentgyörgy.

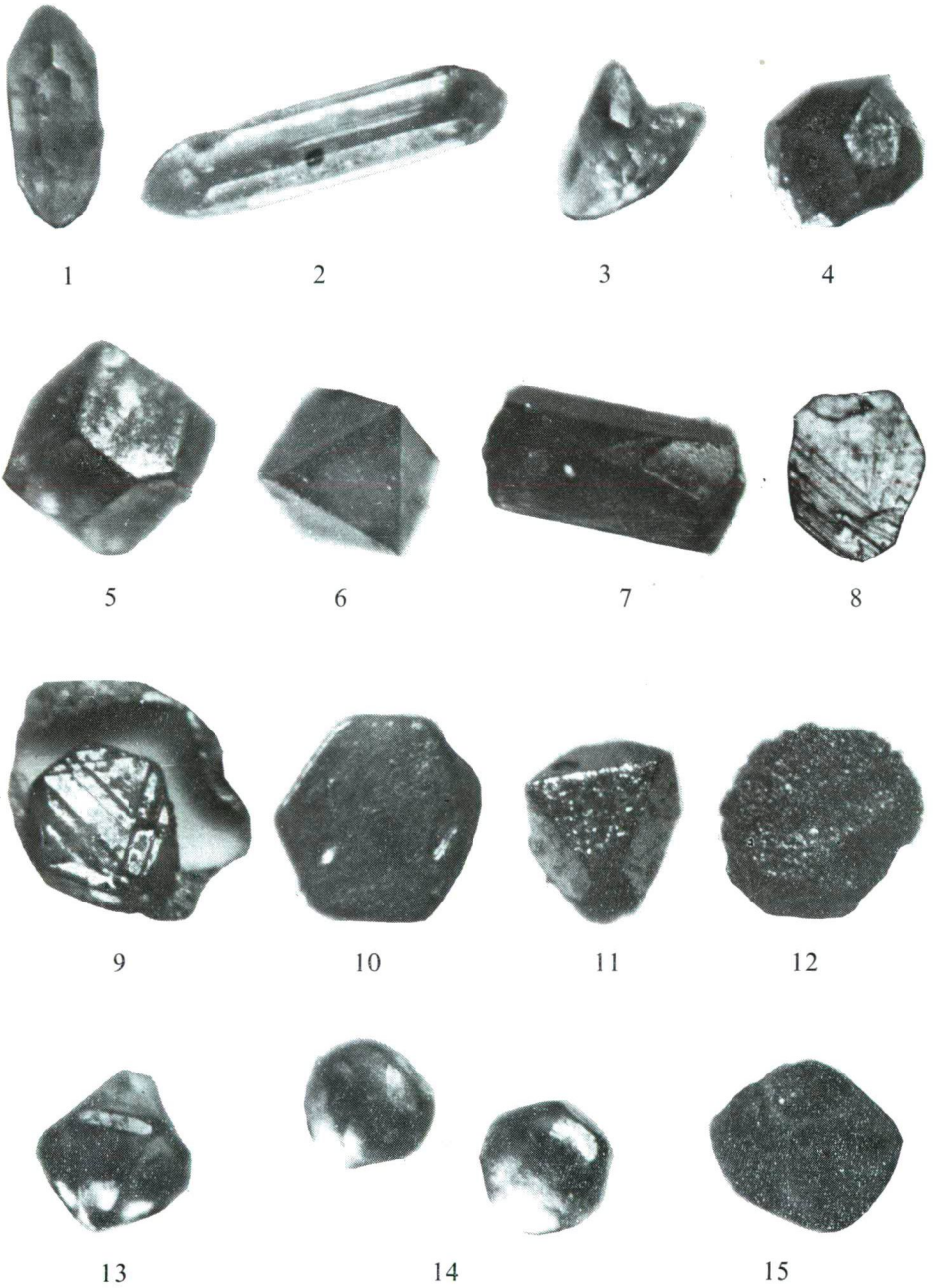

Fig. 2. Some clastic minerals from the settling rest of the bauxite. *1—3.* Zirkon. *4—5.* Spessartin. *6.* Spinel. *7.* Tourmaline. *8—9.* Corundum. *10—12.* Ferriilmenit. *13.* Intact dihexaedral quartz. *14.* Rounded quartz grains. *15.* Internal filling of shells by glauconite.

TABLE 1

Epigenic	Doubly or severally redeposited	Magmatic	Metamorphic
minerals			
Pyrite	Quartz	Quartz	Quartz?
Gypsum	Turmaline	Turmaline?	Turmaline?
Goethite	Spessartine	Muscovite?	Spessartine?
Lithiophorite	Staurolite	Biotite?	Staurolite
Rutile	Ferriilmenite	Ferriilmenite	Muscovite
Ferriilmenite?	Muscovite	Rutile?	Chlorite?
Zircon?	Biotite	Zircon	Spinel
Corundum?	Chlorite	Spessartine?	Corundum?
	Dolomite		Rutile?
	Glauconite		
	Corundum		
	Rutile		
	Zircon		

It is clear from Table 1 that unless the case of the idiomorphic, dihexahedral quartz and also idiomorphic spinel, staurolite, zircon, ferriilmenite and possibly corundum, the immediate origin from magmatic or metamorphic rocks is doubtful, because the heavily rounded (i.e. perhaps doubly or severally reworked) grains of the mentioned minerals are also present. Moreover, the epigenic formation of the zircon cannot be precluded, since epigenic zircon was recorded from other sedimentary rocks (e. g. sandstones) [SAXENA, 1964]. Epigenic zircon formation is suggested by the idiomorphic, fragile, acicular appearance together with the heavily rounded grains within the same sample, precluding here the possibility of transport. The epigenic corundum formation have been indicated (ICSOBA). The epigenic origin for this mineral is suggested by the grains of "graded" structure referred to overgrowing. The ferriilmenite and the dihexahedral quartz can be originated from the Middle Eocene amfibole-andesite tuffs known at Halimba, and from intrusive rocks, respectively. Though the bauxites lack the favourable conditions for epigenic ferriilmenite formation [MINDSZENTY, 1970], even this possibility cannot be rejected. The majority of the minerals can be derived partly from sedimentary (mainly Lower and Middle Eocene and subordinately Mesozoic) rocks, and partly came after a shorter or longer bauxitic weathering, or transported as immediate detritus of siallitic-allitic magmatic or metamorphic rocks. It is worth to mention here the studies of SZABÓ—RAVASZ [1970], who suggested the Middle Triassic volcanic (tuffitic) material as the parent rock of the bauxites of the Transdanubian Central Mountains.

Fig. 3 shows the quantitative distribution diagrams. Within the certain proper weight percent intervals the quantity of the 0,2—0,1 mm fraction is nearly identical within the same horizons of the bauxite body. In the deeper horizons amounts to 0,05%; increasing upwards, where a horizon of 0,05—0,1% value can be recognized. In Profile 1 within the middle portion of the bauxite body a considerable enrichment appears, attaining its greatest value in Borehole Rp—27, but decreasing to 0,1—0,4% on both sides of this borehole. Going further upwards the quantity of the minerals decreases again and attains a value equivalent to that in the basal part of the body. In this upper part the enrichment is occasional (Boreholes Rp—23;

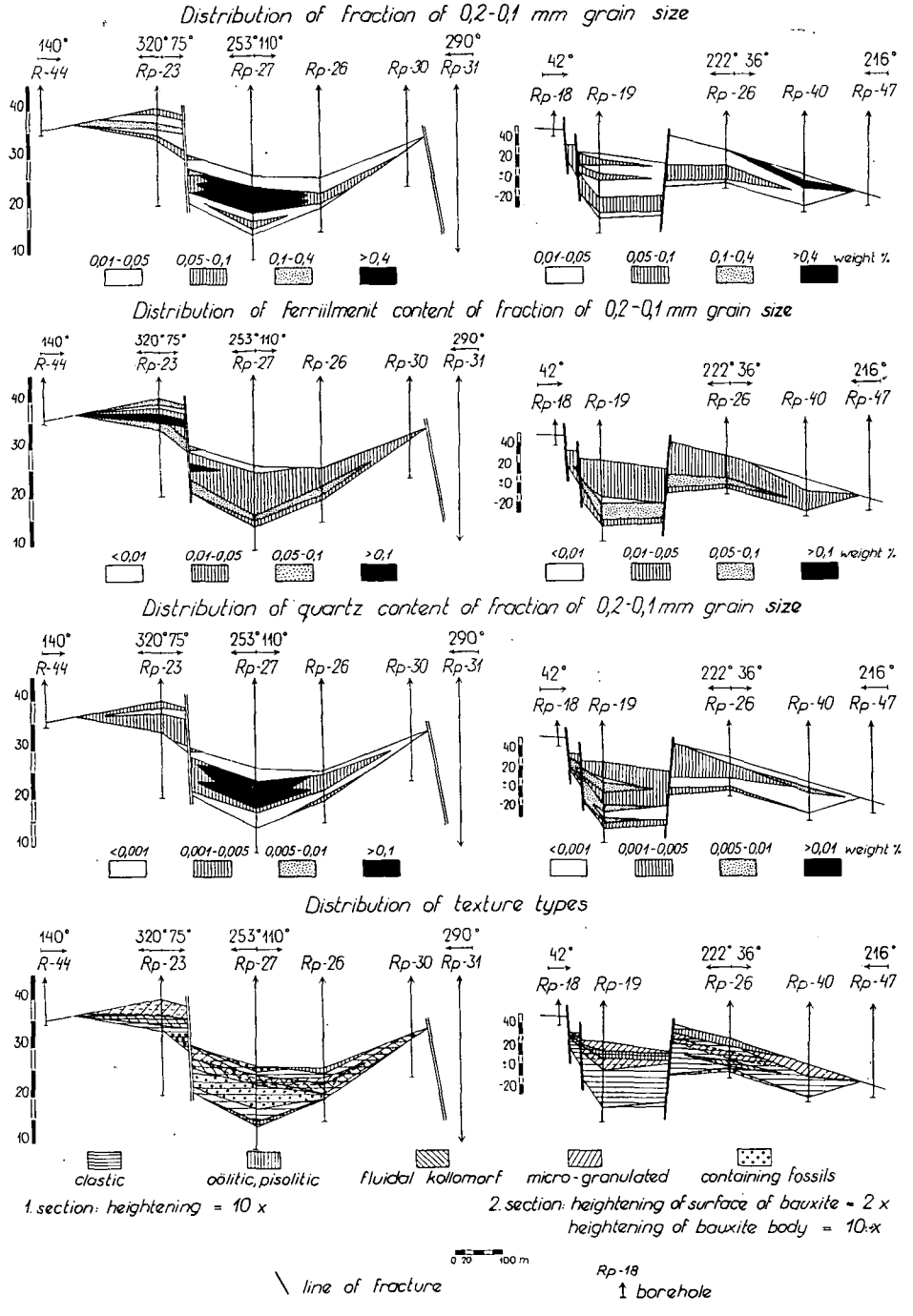

Fig. 3. Distributional sections.

Rp—40) and can be due to the epigenic pyrite content of the grey bauxite and therefore non-detrital in character. The mineral content of the thicker portions of the bauxite body shows further irregularities (e.g. in Borehole Rp—19).

From the minerals of this fraction only the ferriilmenite and the quartz, those of definitive quantity, were studied in detail. The distribution of the ferriilmenite is relatively regular, most common is the 0,01—0,05% quantity. It enriches in the lower part of the bauxite body, and except in Borehole Rp—23, usually decreases upwards gradually. Its distribution somewhat corresponds (especially in Profile 2) to the total amount of the fraction. The distribution of its values are relatively unvarying.

The distribution of the quartz is more changeable as compared to that of the ferriilmenite, and strikingly corresponds to the distribution of the total amount of the fraction.

The distribution of the other minerals — owing to their small quantity — unworthy for figuring, however, remarkable the distribution of the spessartine, being similar to that of the quartz.

Thus in the middle portion of Profile 1 of strike direction appears a remarkable detrital enrichment, and this is traceable in Profile 2 of dip direction. In this belt the detritus consists of quartz, glaukonite and spessartine, with an oscillative distribution of the detritus and the quartz within that. On the basis of the distribution along the profile a detrital transport towards NE direction can be expected, i.e. the belt of detritus of greatest quantity extends in this direction, across Borehole Rp—27.

TEXTURAL STUDIES OF THE BAUXITE

The basis for the textural nomenclature in thin-section textural studies is what have been outlined by BÁRDOSSY—PANTÓ [1970] in connection with their electron microprobe studies. On the other hand the two methods differ in an order of magnitude, i.e. the fine-structural features in thin-sections are indistinguishable, but these are traceable with the microprobe. But similar and even some identical textural types were recognizable in thin-sections and with the microprobe as well.

The identified textural types were: pelitomorphic, micro-grained, collomorphic-fluidal, spotted, brecciated and detrital. These are usually mixed, with a dominant type and some associated subordinate ones. Commonly the micro-grained and the pelitomorphic types are inseparable. This terms bear certain genetical meaning too, suggesting different energetic levels.

The bauxite of the Rákhegy locality is overwhelmingly of detrital texture, severally mixed with collomorphic features as additional type (Samples 20, 23, 37, 44), but subordinately oöides also appear (Samples 31, 20, 32). Pisoides and brecciated texture occured only in Samples 33 and 24. The ball-shaped grains are also common, but characteristically appear exclusively in Sample 32. The spotted texture occurs mainly in Borehole Rp—23. Also subordinate the micro-grained or micro-grained — pelitomorphic textural type, being represented only in Samples 1 and 15. The textural types are shown in *Figures 4, 5* and *6*.

The detailed review of the textural elements is given below.

Bauxitic detritus

Size between 10 and 2000 micron. Most common is the sharp, highly ferritic (hematitic) detritus *(Fig. 4/1a)*. Subordinately, but all in the detrital samples the

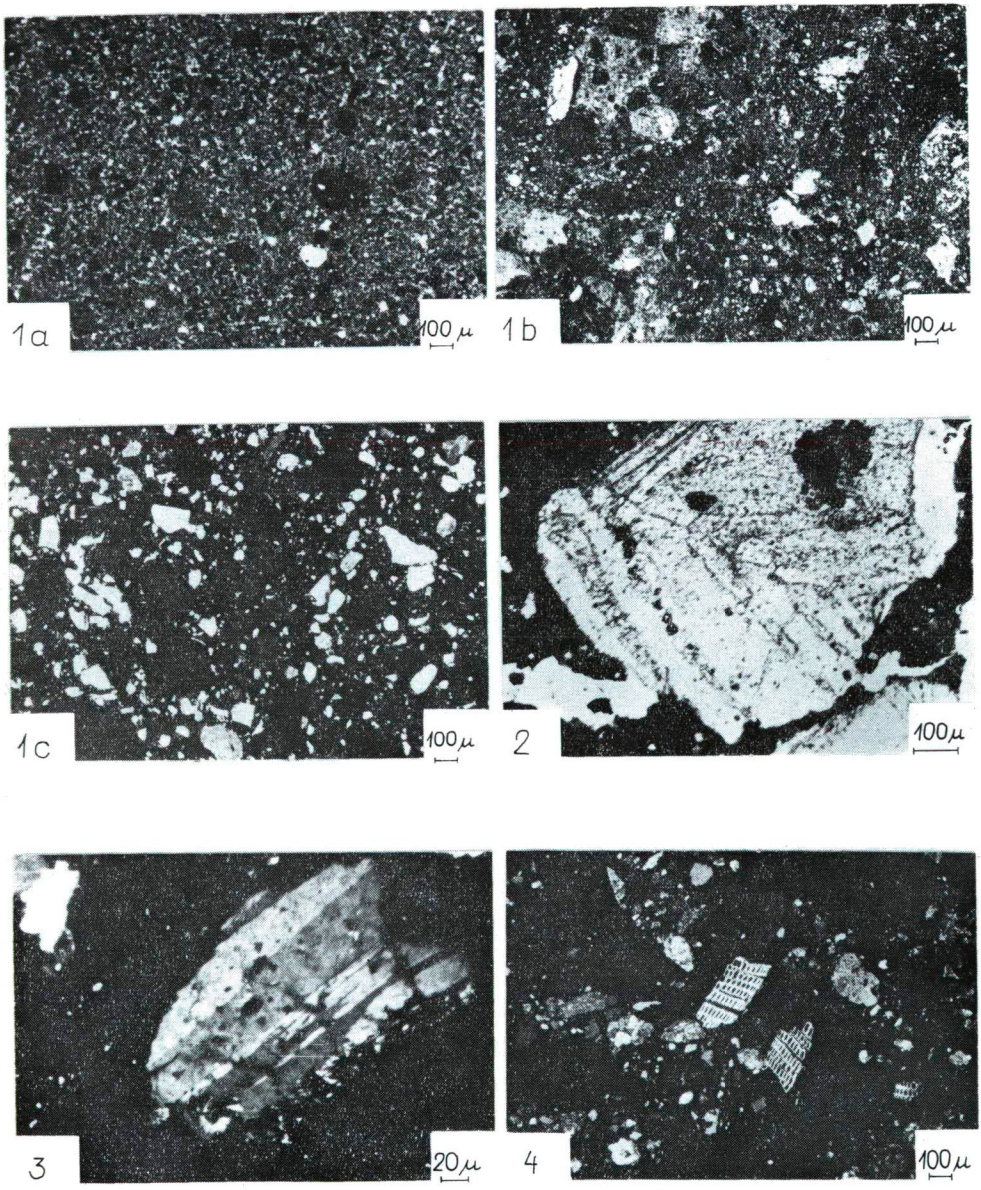

Fig. 4. 1a-c. Bauxite of clastic texture. *2.* Nummulites from the Sample No. 39/b. *3.* Strongly weathered feldspar (Sample No. 24/c.) *4.* Fragments of Bryozoan and rocks (Sample No. 25/a).

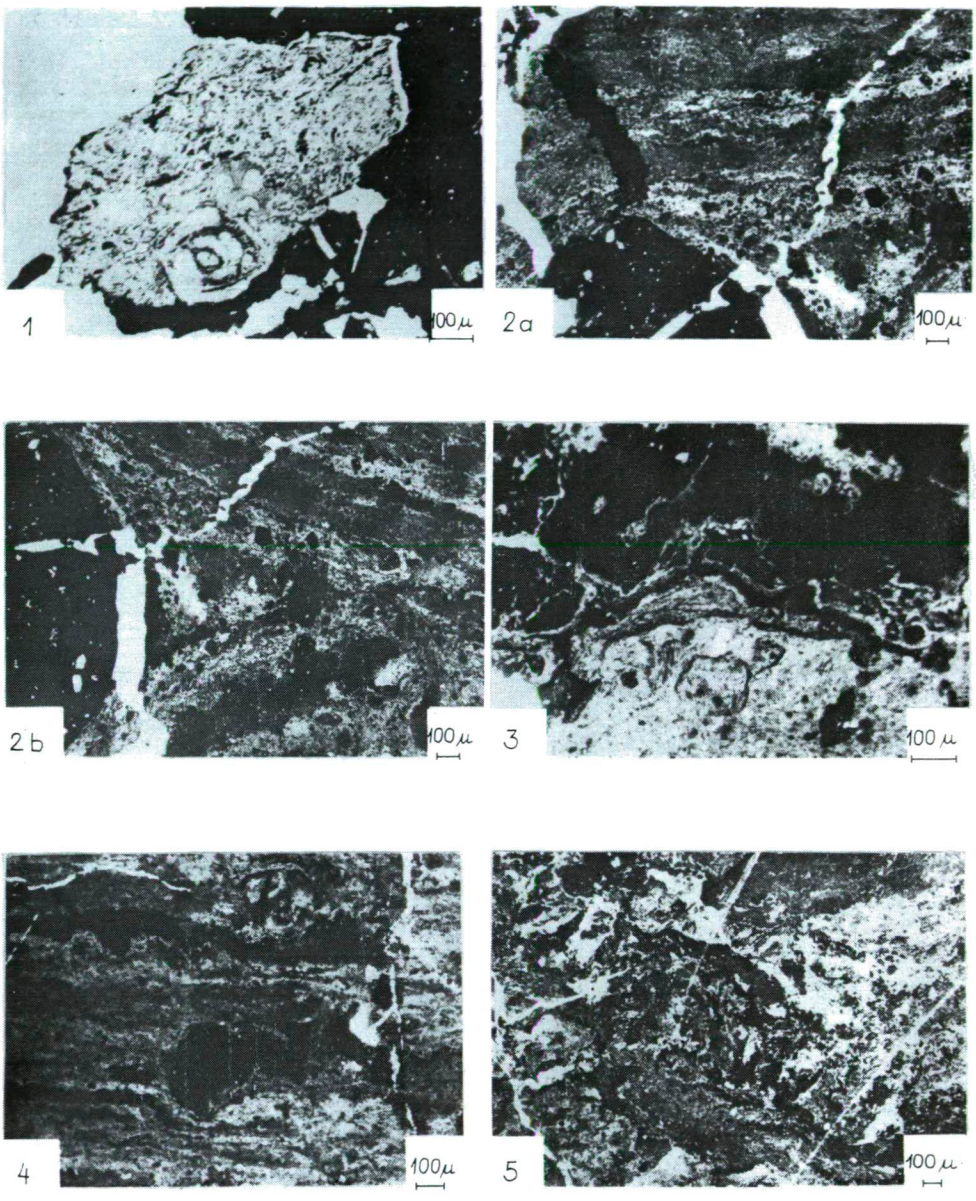

Fig. 5. 1. Fragments of limestone with Miliolina and Bryozoans. *2a-b.* Fluidal texture (Sample No. 37). *3.* Collomorphy precipitation of gel of iron hydroxide (Sample No. 44). *4.* Lamination caused by fluidal texture (Sample No. 23). *5.* Congestion in fluidal texture (Sample No. 23.).

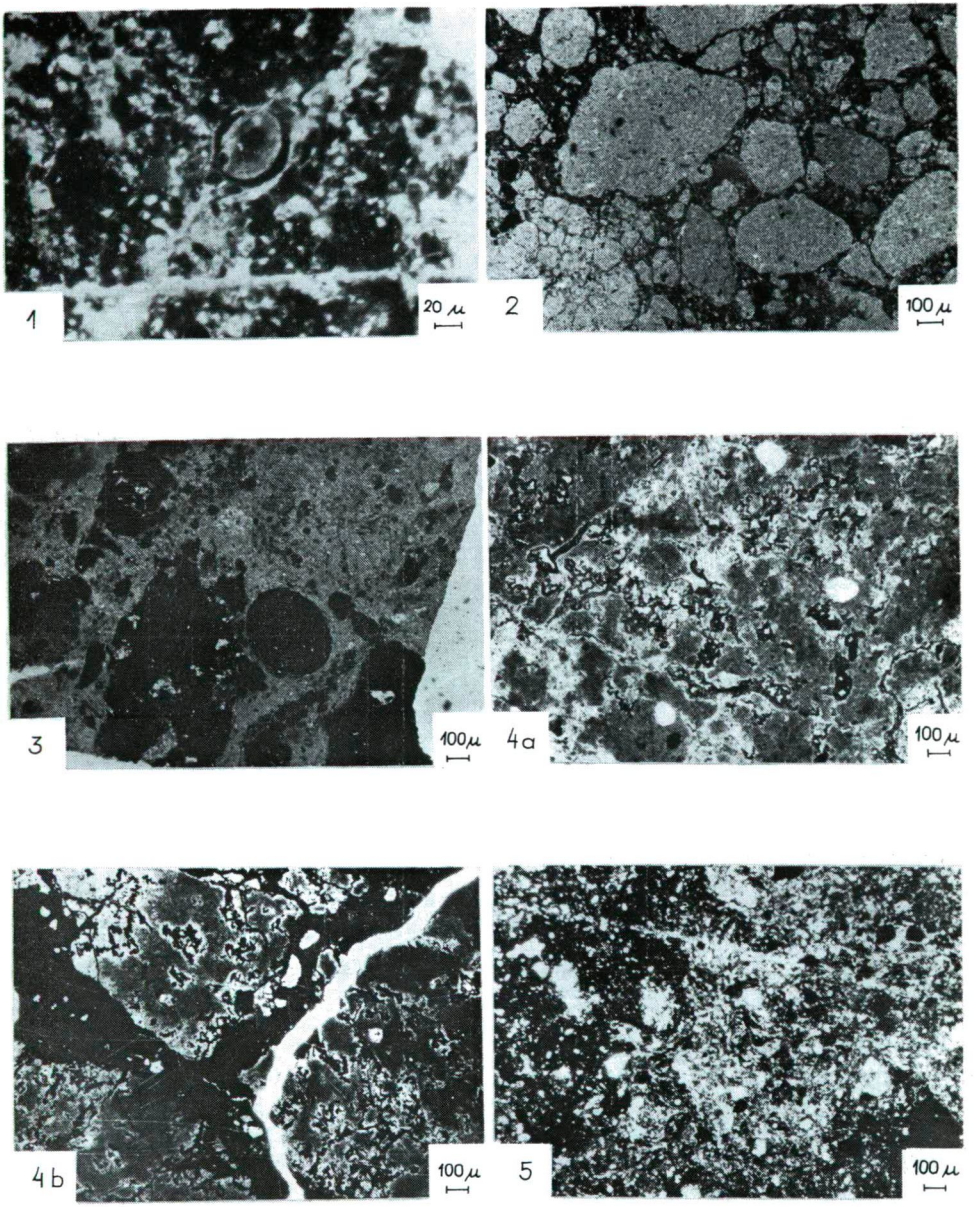

Fig. 6. 1. Oöide (Sample No. 20). *2.* Brecciated texture (Sample No. 24/a.) *3.* Ball-shaped grain (Sample No. 44). *4a-b.* Bauxite with spotted texture (Sample No. 24/a). *5.* Bauxite with kaolinite-contents (Sample No. 32/a).

yellow, yellow-brown, less ferritic detrital also represented, with more rounded shape, showing the more resistant nature of the latter, as compared to the hematitic one. Secondary iron layers encrusting some detrital grains also can be recognized.

Ball-shaped grains

Non characteristically, but frequently represented, especially in the samples from deeper portions. The majority is considerably of ferritic, but while the detrital grains are of hematitic, these spherical grains are often represented as brown, goethitic nodules *(Fig. 6/3)*. Size between 100—600 micron. The overwhelming angularity of the detritus seems to suggest a minor, short-distance, or an autochtonous redeposition, and the subordinate quantity of the shperical grains, *i.e.* the more rounded bauxitic detritus do not contradict this.

Non-bauxitic detritus

In the middle part of Borehole Rp—27 and in the basal part of Borehole Rp—26 appears a considerably clastic, fossiliferous zone *(Fig. 4/1c—4)*. These fossils (nummulites, miliolinids, other small forams, bryozoans) date the bauxite redeposition whithin the Eocene. The oldest overlying layer is of Lower Lutetian, thus the redeposition can be ranged into the Early Eocene or at the early Middle Eocene. Most likely the intralutetian denudation [KOPEK—KECSKEMÉTI, 1965] played an important role in this process. The unrounded nature of the detritus (calcite, dolomite, quartz, spessartine, rock-fragments) as well as the presence of calcitic shells indicate short-distance redeposition. On the basis of the basal appearance of the Eocene clastics in Borehole Rp—26, it is reasonable to conclude a redeposition of the underlying beds associated with the bauxite originally laid down on Eocene foot-wall.

Fluidal-collomorphic textural elements

Most common are the textures giving proof of a previous flowing movements in a presumed plastic state of the deposit *(Fig. 5/2a—b)*. In some cases appears stratification *(Fig. 5/4)*, in other cases the matrix "flows round" bigger bauxitic detritus. This phenomenon can be due to the impression of bigger grains into the matrix, or to the flow of the matrix transporting finer detritus round the bigger grains as well. Both of these causes can be recognized in Samples 20, 23 and 27. Collomorphic elements suggesting gelate state material movement and rhythmic precipitation can also be recorded, and can be originated from the presumably less viscous material *(Fig. 5/3)*. Occasionally congestive structure is also appeared *(Fig. 5/6)*. The matrix of the fluidal textural portions "carrying" the detrital grains is usually lighter (yellow), i.e. poorer in iron.

Oöides, pisoides

Pisoidic material exclusively appears in (uppermost) Sample 33 of Borehole Rp—26. The material of the pisoides is pyritic grey bauxite. The pisoides could indicate the beginning of the overflowing of the area by water. The sporadically occuring oöides partly are just initiatives *(Fig. 6/1)*, without distinct nuclei, with hematitic central part. The quantity and the primitive character of the oöides indicate a subordinate or autochtonous redeposition.

Brecciated texture

It is the characteristic textural type of Sample 24 *(Fig. 6/2)*. Probably it can be due to a post-, or final-redepositional process, because this kind of fragmentation impossible within a plastic material.

Spotted texture

This term have been used in the macroscopic descriptions, too. It refers to the irregular alteration of the light (poor in iron) and darker (richter in iron) spots in the bauxites. This type is well recognizable in several samples of Borehole Rp—23 and in Sample 24 *(Fig. 6/4a—b)*. In some places the light spots are penetrated by meandering small ferrous veins. This probably shows a diagenetic iron-mobilization. Thus the iron have mobilized during the formation of the spotted texture partly remained within the bauxite body and subsequently precipitated through the changed physico-chemical circumstances.

Kaolinite

The presence of the kaolinite considerably effects the rock-texture, though the kaolinite in itself is not an independent textural element. It is represented, with variable quantity, in the majority of the samples, forming nodules, grain-congeries, branching forms and disseminated grains. The nodules are everywhere present, the other forms are dominant in the lower, kaolinic portion of the bauxite body *(Fig. 6/5)*. The grain-size is 1 to 10 micron, the nodules are of several hundred micron in size. Vermicular forms are also common. Whether the kaolinite formed after or before redeposition hard to decide. The kaolinite of the detrital grains presumably came together with the detritus, but the disseminated and amorphous kaolinite of the lower kaolinitic bauxite is an autochtonous precipitation.

Fig. 3/d shows the distribution of the textural elements. The basis is the symbol of the detritus, while the symbols of the other textural elements (in the case of mixing) are taken onto this. Separately signed is the fossil layer. The distributional regularities recognized in the profiles are as follows:

1. The pisoidic textural element exclusively occurs in the grey bauxite, in the surface of the bauxite body, within a single borehole (Borehole Rp—26). In strike direction this is the deepest point of the bauxite body.

2. Oöides occur characteristically in the upper and in the basal part (Boreholes Rp—19 and Rp—27, respectively) of the bauxite body, exclusively in the detrital bauxite.

3. The fluidal-collomorphic textural elements appear in the middle and upper part of the bauxite body, exclusively under or at most mixed with the micro-grained bauxite (Borehole Rp—27). In a profile along strike direction it runs through the whole bauxite body, but in profile of dip direction it appears only in a single borehole (Borehole Rp—26).

4. Bauxite of purely micro-grained texture occurs only in the uppermost parts (Rp—19, Rp—40), where it forms the grey pyritic bauxite. In mixed types it appears also in the upper horizons and within both profils it runs through nearly the whole bauxite body.

5. The considerably detrital bauxite containing Lower or Middle Eocene fossils and rock-fragments can be found in the middle and lower parts of the profiles. In Borehole Rp—27 it occurs with a considerable thickness (6 metres), on the other hand in Borehole Rp—26 it appears only in the basal part. The pyritic bauxite of Borehole Rp—27 also contains mollusc shell-fragments, thus it can be considered as of detrital too, but it seems to be more possible that these fossils have derived from the swamps overlain the bauxite body in Middle Eocene times.

6. In the profiles some depositional tendency is also can be recognized. Namely the basal part of the bauxite is of considerably detrital (oöidic and partly fossili-

ferous). The detrital character partly constant and partly decreases upwards, and then appear the mixed types to the detriment of the detrital type. In some places the mixed types extend up to the surface, in other places the detrital material tends to subordinate, and even absent. Exception to the rule is the pisoidic bauxite of the uppermost part in Borehole Rp—26.

CONCLUSIONS

On the basis of its size and dimensions the bauxite body of Rákhegy deposited in an elongated, platter-like depression, with its possible deepest point in the vicinity of Borehole Rp—26. The material carried into this depression presumably derived from the erosional products partly of rocks (dolomites, limestones, marls, even previously bauxitized clays) of the surrounding area, and partly of rocks (metamorphic schists and magmatics) of distant regions. According to the presence of bauxitic detrital grains in the bauxite body, a redeposition of a previously deposited bauxite also can be supposed. Taking the textural features into consideration on the basis of the general picture of the distribution, a transportation belt of SSW to NNE direction can be assumed. The middle part of this belt is intersected by Borehole Rp—27. Taking the Eocene detrital material of Borehole Rp—26 into account, the direction of this belt can be of SE to NW. Presumably both are proper directions.

The bauxite of Rákhegy texturally is almost completely of detrital origination. This detrital character is a result of autochtonous redeposition in one hand and detrital afflux in the other. The more considerably detrital belt recognized within the bauxite body presumably shows the line of stronger water current. This detrital character of the Rákhegy bauxite contradicts the "terra rossa" theory of bauxite formation. The downward increasing detrital character supports the parautochtonous theory [BONTE, 1970]. According to this theory, in the course of the bauxitic material accumulation (*i.e.* during the infilling of the basin) the intensity of the water currents decreased, then the area was covered by intermittently stagnant waters, facilitating by the loosening the bauxitic material the autochtonous redeposition. Such a redeposition is also proved by the presence of great amount of unrounded bauxitic detritus. In this stage of bauxitization the bauxitic material is partly already in hard, but partly still in plastic state. During the stage of loosed material content the bauxite turned into of detrital fluidal character. Since these phenomena can be recognized within the major part of the bauxite body, it is reasonable to suppose a periodical accumulation of the bauxitic material, specially as the subsequent loosening within a thick bauxite deposit is hard to conceive. It is suggested also by the distribution of the detrital fraction by horizons, showing the variable intensity of the transportation. The small number of the usually primitive oöids found in the bauxite, as well as the dominantly boehmitic character suggest that there was no considerable water infiltration causing strong outwashing in this area, thus pisoidic bauxite could have not formed in greater quantity. The micro-grained, pelitomorphic, scarcely detrital bauxite of the uppermost part of the body deposited in partly stagnant water.

The bauxite accumulation was followed by pyritization, iron-mobilization. The hydrogene sulfidic substance of the foregoing swamp interval of the Upper Lutetian transgression led to formation of grey bauxite. On the other hand the subsequent tectonic movements brought certain parts of the bauxite body into strongly oxidative environment, oxidizing in this way the pyritic bauxite material, and — in

the way of sulfidic acid formation — caused iron-content mobilization within the bauxite material situated in deeper horizons. Conclusively the bauxite of Rákhegy is a result of the autochtonous bauxitization of bauxitic clayey wash, and the redeposition of previously formed bauxite. On the basis of its detrital mineral content, all of the rocks can be assumed as parent rock which were exposed to the erosional processes during the bauxite accumulation (carbonate rocks, clays, sandstones, metamorphic and magmatic rocks and their detritus).

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A REVIEW OF THE TRIASSIC IN HUNGARY

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Most of the Triassic sequences, making up the bulk of the Hungarian Highlands and widespread in the basement of the Tertiary basins of the Pannonian Mass as well, are characterized by purely Alpine facies. "Germanic features" in the Middle, terrestrial and lacustrine sedimentation in the Upper Triassic can be proved alone in the Mecsek Mountains. To an early and lasting break of sedimentation, however, it came in the Villány Mountains only.

The Early Triassic transgression in Hungary started from that relatively narrow, latest Permian sea-branch extending from the junction of the Southern Alps and Dinarides northeastwards across central Transdanubia, the northern Great Hungarian Plain and the Bükk Mountains up to the northern Gömörides. Accordingly, the Lower Triassic of this belt overlie the purely marine respectively lagoonal-hyperhaline Upper Permian with more or less distinct changes in lithology and palaeontology, but without any detectable unconformity. The former is the case in the Bükk Mountains, the latter in the northern part of the Balaton Highland respectively in the southern foreland of the Vértes Mountains. On the contrary, both in the southwestern part of the Balaton Highland and in the Villány and Mecsek Mountains, the two systems are set apart by a striking unconformity. Very strongly that is expressed in the latter ranges by the coarse basal conglomerate of the widely transgressing Jakabhegy sandstone complex. Unfortunately, the separation of the Lower Triassic and Late Permian sequences is not perfectly solved either in the Hungarian stretch of the Southern Gömörides or in the Great Hungarian Plain as yet. This is partly due to the similarity and the poor fossil content respectively to the deficiency of information on the sequences in question.

In Hungary the upper boundary of the Triassic system is drawn between the Rhaetian and the Lias on the following grounds:

a) The Rhaetian, wherever detectable, is closely interconnected, in all facies, with the deeper member of the Upper Triassic.

b) It is true that the Rhaetian of the Bakony and Mecsek does not show up a sharp boundary with the Lias. On the other hand, the Triassic is separated from a little higher level of the Lias both in the northeastern parts of the Transdanubian Central Mountains and the northern part of the Gömör Karst by an erosional unconformity due to light epeirogenetic uplift. This unconformity falls everywhere unambiguously between Norian-Rhaetian and Liassic formations documentable by fossils. And the Rhaetian stage, either complete or incomplete, has not in a single case been observed above this overlap.

In accordance with the transgression that invaded the Latest Permian emergent land portions characterized by erosion and terrestrial sediment accumulation, the Seisian substage of the Vértes, Gömör-Rudabánya and the middle and southern Great Hungarian Plain as well as of the Mecsek and Villány Mountains is announced by the predominance of red and green detrital sediments whose source may have been formed first — at least in part — in the Permian as an unconsolidated detrital material which was subsequently redeposited and resedimented in a shallow-water environment.

On the contrary, the Lower Triassic of Central Transdanubia begins with dolomitic-marly sediments, that of the Bükk Mountains, in turn, with light-grey oölitic limestone banks. Reddish or purple sandstone beds in this belt appear in the lower or middle part of the Campilian substage only. Traces of this inflow of Campilian coarse detrital material occur otherwise farther north in the Lower Triassic of the Gömör Karst as well. It seems, however, a general rule that in whole Hungary the topmost of the Lower Triassic consists of grey to dark-grey, thin-bedded or laminated limestones covering ever finer marls, anhydrite-bearing beds or early-diagenized dolomites.

The Middle Triassic is dominated everywhere by diversified dolomite and limestone facies interbedded with several levels of submarine volcanic products. The hughest volcanic masses are known to occur in the Bükk Mountains (porphyrite sequence of the Szent Istvánhegy in the Middle Anisian; diabase of Óhuta and quarz-porphyry of Bagolyhegy in the Ladinian-Carnian). Here the volcanism seems to extend well into the Carnian stage. Minor quartz-porphyry bodies of Ladinian age occur in the Rudabánya Mountains, too. Elsewhere (Gömör Karst, Balaton Highland, Mecsek), just relatively thin intercalations of tuffite could only be identified (e.g. the "Pietra verde beds" of the Balaton district).

The Ladinian stage is characterized by the grading of the lithofacies into more and more variegated types of sediment. In the Villány Mountains the sedimentation was stopped for a considerable span of time. In the Mecsek Mountains an upwards more and more sandier slate sequence with plant remains leads through into the regressive Upper Triassic. As a contrast, the Ladinian shales of the Bükk and Rudabánya Mountains are indicative of a deepening sea.

In genetic relation with the volcanic intercalations radiolarites, respectively limestones and dolomites with nodules of chert appear here. On the other hand the dolomite with *Diplopora annulata* in the Vértes and Buda Mountains, respectively the Wetterstein limestone and dolomite in Gömör and Rudabánya signifies extensive fields of lime-secreting algues, on some places coral-reefs, too.

The Upper Triassic of the Balaton region begins with the Upper Marl sequence of Carnian age, whose members (Füred limestone, Marls with Estheria, Limestone with *Trachyceras austriacum*, Marls with *Nucula* and *Lima*, Sándorhegy limestone) are enumerated also on the Table 1 in detail. Apart from this, however, the Upper Triassic sequence of the Central Transdanubian Mountains is filled up by "Hauptdolomit" (Main dolomite) or Dachstein limestone. From Vértes toward NE they are underlaid by the Mátyáshegy limestone, respectively Mátyáshegy dolomite, both bearing nodules of chert. The Dachstein limestone, however, that fills up only the Rhaetian in the Western Bakony, appears toward NE in more and more deeper horizons. Thus it pushes out the "Hauptdolomit" showing still to be Carnian or Norian in the Bakony and Vértes, already nearly totally in the Buda Mountains.

The Kössen facies that appears in the Western Bakony in form of intercalations

and lenses between the Norian "Hauptdolomit" and the Uppern Rhaetian Dachstein limestone, refers to locale deepenings of basin. In consequence of the formation of the Dachstein limestone in a shallow water environment, a minor uplift was already sufficient to produce the breaks of sedimentation on the boundary Triassic Lias in the NE parts of the Central Transdanubian Mountains.

The Carnian stage in the Bükk Mountains is filled up by several varieties of limestone (with and without chert-nodules, or built up by corals) that are joined with the volcanic products mentioned above. Here the Norian is represented by grey limestones with *Monotis salinaria*. The same in Gömör is represented by red Hallstatt limestones overlaying the *Halobia*-bearing Carnian limestones of Szöllősardó.

Irrespective of some parts of the Bakony, Vértes, Gerecse and Pilis, the youngest part of the Triassic, together with the Jurassic, was subsequently eroded. Probably, the age of denudation is undergone a change from area to area.

Unlike the limestone facies predominating the more northern areas, the Upper Triassic of the Mecsek is made up entirely of a thick fluvial-lacustrine sequence of the Karolinavölgy sandstone. This regression, however, was followed, from the Hettangian on, by a paralic sedimentation whose scene deepened after several oscillations gradually causing repeatedly the formation of coal-beds of excellent quality. In the Mecsek bay, however, landlocked as it was in the W, S and N, the sedimentation did continue even after complete isolation from the seas, whereas in the Villány Mountains a break in sedimentation encompassing the interval from the Middle Ladinian up to the Middle Jurassic can be observed.

The Triassic sequence which is proved as the most particularly divisible by biostratigraphic methods, appears in the Balaton Highland and the Bakony Mountains. Since 1913, however, the rich collections of fossil published in the famous Balaton-monography avoided a complete revision despite of the large numbers of the artificial outcrops made in the last years. That is all the more to regret, because there is a possibility in whole Hungary only here to lean on an uninterrupted succession of ammonites in the interval Middle Campilian/Carnian.

Among the ammonite zones appearing in Hungary that of the *Tirolites cassianus* has the widest extension. Outside the Balaton district it occurs, that is to say, in whole Hungary. In the Mecsek Mountains the zones of *Paraceratites bi-* and *trinodosus* present oneself that are besides proved only in the Balaton Highland till now: the reason for this fact is evidently to look for the conditions of sedimentation.

In the Villány region the ammonites (and the conodonts, too) are totally missing. Both in the NE parts of the Central Transdanubian Mountains and in northern Hungary the ammonites of certain zones occure in lenses only. Therefore one had already long no choice but to use also other fossil-groups (e.g. dasycladacees, brachiopods, pelecypods and gastropods, newest sporomorphes, foraminifers and conodonts, too) to the subdivision of the Triassic sequences. On support of all these fossils the stratigraphy of the Bükk, and Gömör, further the Mecsek and Villány complexes was elaborated at last time. The greatest results, however, were achieved by the treatise of E. VÉGH–NEUBRANDT on the *Megalodonts* of the Transdanubian Dachstein-limestones and "Hauptdolomit"-es.

On the Table 1 we attempt to summarize the valid names of the most important stratigraphic units of the Triassic in Hungary with their chronological and territorial distribution, that way they were compiled for the new edition of the Stratigraphical Lexicon of Hungary.

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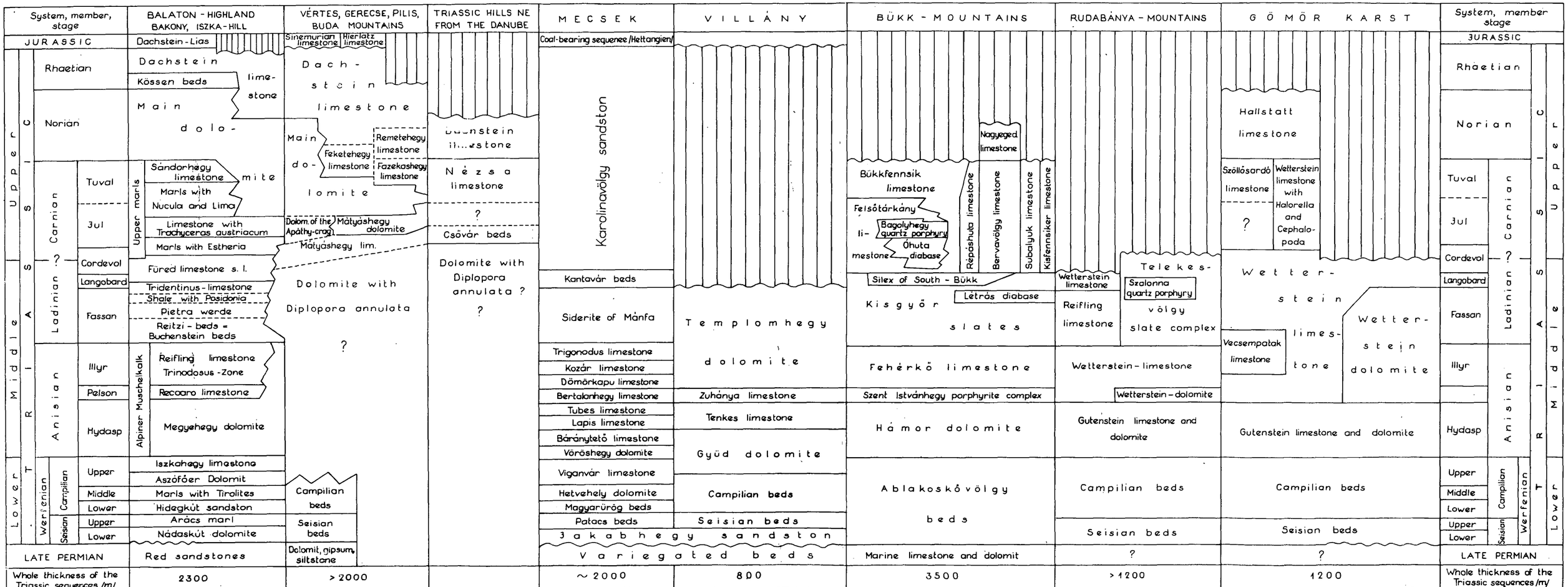
REVIEW OF THE TRIASSIC SEQUENCES IN HUNGARY



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SEDIMENTARY FEATURES OF THE TRANSGRESSIVE NEOGENE SEQUENCES OF THE SOUTHERN GREAT HUNGARIAN PLAIN*

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L. LÓCZY SR. [1916] was the first, to be followed later by K. TELEGDI ROTH [1929, pp. 135—138], who drew the consequences of the fact that in the southern and southeastern marginal mountains surrounding the Pannonian Basin the Mesozoic or pre-Mesozoic basement is overlain immediately, with absence of the Palaeogene, by Middle Miocene marine sequences. The essence of their conclusions that the Neogene seas had from the Upper Mediterranean on gradually inundated the Palaeogene land wich occupied the greatest part of the today's Great Hungarian Plain is confirmed by the newest syntheses [G. HÁMOR, Á. JÁMBOR, 1971; L. KŐRÖSSY, 1968; M. SZÉLES, 1971]. The development is still incontestably remarkable, for in the light of numerous wells undertaken in the last four decades, a number of details of LÓCZY—TELEGDI ROTH's ideas has now become a tangible reality. On account of this, our knowledge of the age, nature, dimensions and trends of Neogene transgressions has been considerably widened. As evidenced convincingly by the regarding isopach maps, the Great Hungarian Plain's Neogene basin must have consisted of several subbasins wich subsided at varying rates. Lithological investigations, in turn, testify to the fact that these subbasins had been separated by islands of different size before the subsidence became an overall phenomenon. In a number of cases excellent hydrocarbon traps have developed in the pseudo-domed hanging sequences of these former islands that, in spite of their subsequent burial, still remained higher compared to the surrounding basement.

The fate of the islands was naturally different in dependence on their position. Some of them were inundated already during Tortonian transgression and at the time of the expansion of the Early Pannonian inland sea they formed already only subaquatic ridges (e. g. one of this kind seems to have been the basement of the Kiskundorozsma and Szeged structures). On the other hand, in the case of the Algyő structure a little farther east, only the western limb could be shown to include Miocene deposite, but the overwhelming majority of the core of the structure still formed an island at the beginning of the Pannonian. Lower Tortonian and Lower Pannonian sedimentation are not only chronologically separated from each other, but there is also a considerable facies-difference between the two due to dimensions, connections, salinity, fossil content, etc. In spite of this fact (at least in the area men-

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tioned above), a striking similarity can be recognized between the sedimentary features of the transgressive sequences of the Early Tortonian sea on the one hand and the Early Pannonian inland sea on the other.

1. The *Tortonian sequence* begins with a massive, frequently breccia-like basal conglomerate overlying a basement consisting of cristalline schists at Dorozsma and of crystalline schists and Lower and Middle Triassic sediments at Szeged (Plate I, *Fig. 1* and *2*). Poorly sorted and rounded, attaining 5, 7 or even 12 cm in diametre, the coarse pebbles of this conglomerate are embedded in coarse-grained sandstones or fine-grained conglomerates. The rock grains reflect the composition of the environment of their accumulation. Accordingly, at Dorozsma they consist of chloritic micaschist and quartzite. At Szeged (at least in the more northern boreholes), however, the fragments of metamorphite fall into the background against the grains of the dark-grey Middle Triassic dolomites, purple-red Seisian sandstones and green Werfenian shales and dolomitic marls, and in the poor sandstone cement dolomite and quartz predominate as well. However dissimilar to be the rock of Szeged looks as compared to that of Dorozsma, the variegated colour and composition have obviously been caused merely by local changes in the lithology of the source area, changes reflecting the combined effect of pre-transgression tectogenesis and erosion. Despite their substantial differences, the two rocks must have been produced by a rapid deposition under essentially the same environmental conditions.

Above the breccia-like basal conglomerates the Szeged oil wells have uncovered a member, that may be named as the whole a fine conglomerate, whose well rounded pebbles are enclosed in a light-grey, ill-sorted, poorly muscovitic and usually limeless dolomite—quartz sandstone (Plate I, *Fig. 3, 4*; Plate II, *Fig. 1—4*). The pebbles vary between 2—15—36 mm in diametre, though sometimes attain even >70 mm. For the most part, they consist of dark-grey Middle Triassic dolomites, for the smaller part, of quartzite, whereas the Werfenian and crystalline schist pebbles are sparse and small, with a max. diametre of 6 mm. Between heavily gravelly details there are lenses and sections, usually irregular and characterized by a relative enrichment of the cement. Although good bedding planes cannot even here observed, the pulsating alternation of gravelly and sandy details is nevertheless an indication of a graded bedding trend (Plate II, *Fig. 3*). For the lack of perfect grading, the turbulence of the settling medium, continuous, but barying as to intensity, seems to have been responsible. The thicker gravel streaks and lenses are obviously the results of temporary increase of sediment production and transport. Frequently, however, sandstone-filled, erosion-made cavities sink into the gravel bands (Plate II, *Fig. 1*). The distribution of the coarser sand grains and pebbles in the poorly sorted sandstones overlying the gravel bands often displays a "mesh-like pattern" indicative of horizontal vortices (Plate I, *Fig. 3—4*, Plate II, *Fig. 1—2*). The centre of each "mesh", more or less circular in cross-section and of 1,5 to 3 cm in diametre, is usually filled by finer fractions of sandstone, though a few, less coarse grains may also here occur. The grain size, however, increases towards the periphery of the meshes so that the coarsest grains are always situated on the most external side of those. Both the erosion channels and the mesh-like structures testify to a strirring up and displacement of the sediment formerly settled down. The vertical and oblique vortices scourring the bottom picked up the grains already settled down and carried them away; these of subhorizontal axis, however, lifted the sediment on their ascending branch and dropped it on the descending one. Since the velocity of the water is along the outside of the vortex is higher than in the inside of that, the

distribution of the grains of the mesh-like structures has developed in accordance with this. The scenery of the phenomenon must have been an abrasion plane brought about during the progress of the transgression whose continuous water movement rendered possible partly the disintegration and rounding of the produced debris, partly the formation of the above-mentioned turbidity structures. With the increase of the distance to the coastline, however, the intensity of water movement connected with the surf zone generally decreased and, in accordance with this, with the intervention of finer and finer grain fractions, a more and more perfect graded bedding could develop (Plate II, *Fig. 4*). The resultant shallow-water turbidities, with an additional rapid decrease in grain size, will pass into black marls through sandstone and siltstone, relatively thin and partly massive and poorly graded, partly showing up graded or composite bedding.

The Tortonian marl is a formation of euxinic character, more or less de-clay-mineralized during diagenesis, consisting of alternating fine-grained sands, siltstones, marls and limestones and containing both bacteriopyrite and its limonitic weathering product as well as a little organic matter (Plate III, *Fig. 1—2*). Frequently, even the lime-rich members are interrupted by quartz- and muscovite-rich, fine laminae. Because of its fine-bedding, locally some folding indicative of subaqueous slumping or sediment-flow can be recognized (Plate III, *Fig. 2*). The marl sequence evidences the sudden decrease of the rate of the sedimentation along with a considerable refinement of the grains. All these facts, together with other sedimentary features, indicate the coastline to have been displaced far away and the basin to have rapidly deepened. Containing *planctonic foraminifers,* the marls can be considered the sediment of a quiet, offshore environment rather than that of a more or less land-locked bay.

The sediments of the Tortonian sea overlying the marl sequence have been eroded. It looks probable, however, that above this sequence an alternation of laminae of black argillaceous siltstones and light-grey, small-grained sandstones ought to follow, similar to those found in the well Hódmezővásárhely—1. The sedimentary structures of the latter remember that of the higher part of the Lower Pannonian, with frequent deformations due to subaqueous slumping (Plate III, *Fig. 3*).

2. The *Lower Pannonian sequence* is introduced by two facies replacing each other.

At the beginning of the Pannonian, on the margins of the elevations still forming islands, basal conglomerates and sandstones similar to those of the Tortonian, coarser at the base and gradually decreasing in grain size up in the profile, though always poorly graded and poor in calcium carbonate, were deposited. The composition of these sediments is controlled by the lithology of the basement. This occurs in the studied area only on the limbs of the Algyő structure and following the local conditions, its substance is identical with that of the underlying crystalline schist basement (pegmatite, quartzite and garnet-bearing chloritic schist: Plate III., *Fig.4*; Plate IV. *Fig. 1*). The coarse conglomerates and sandstones vary in proportions from area to area. This sequence differs from the Tortonian basal formation mainly by the relatively rapid decrease of the grain size. Responsible for the pinching out of the sandstone-dotted fine conglomerate bands, this phenomenon can be explained either by that the rocks of the source area have been more liable to chemical weathering, or by the relatively low abrasion energy of the Early Pannonian inland sea, or by a combination of the two. At any rate, no wide abrasion terrace that might

have ensured a heavy rounding for the majority of the coarser grains had been formed there at that time.

However, this fact as well as the sudden subsidence of the Algyő island seems to account for the observation that the basal detritus of the Lower Pannonian is separated from the overlying dark-grey to black marls and limestones merely by a few meters of grey fine-sandy, calcareous siltstone. Although the transitional siltstone sequence lacks any good bedding plane, on account of the recurrence of the coarse sandstone and grit bands and the "cloudy distribution" of the coarser grains atop it does yet exhibit a distinct graded beding (Plate IV. *Fig. 3*). And in order to avoid any doubt as to the shallow-water turbidite nature's being due to the turbidity of the sedimentary environment and to the repeated stirring up of the clastic material streaming in from time to time from the coasts, let us point out that in some samples even the mesh-like eddy structures described above from the higher parts of the Tortonian basal conglomerates can be recognized. Although these do not attain the size of the Tortonian structures and though the "meshes" form just a single row, the genesis of the phenomenon is, perhaps exactly therefore, all the more clear (Plate IV, *Fig. 2*).

The dark-grey marl and calcareous marl sequence, of slightly brownish shade sometimes, is similar to the Tortonian marl sequence both in colour, organic contents, pyrite or limonite contents and the locally recognizable, discontinous horizontal lamination. Exactly for this reason it can be distinguished undoubtedly from the Tortonian marls only on the basis of its foraminiferal sterility, respectively contents of *Congeria* or *Limnocardium,* in spite of the fact that every variant of it contains essentially more detrital material (quartz and muscovite grains) as compared to the formers. Its lamination is usually connected with graded bedding (Plate IV, *Fig. 4*). The marls and calcareous marls of the wells Algyő-17, -19, -27, -88 and -90 rest with spreading transgression, directly on the crystalline basement. In the basin portions, subsiding more rapidly and thus deeper, between the islands, where the littoral conglomerates and sandstones are also missing, it occurs as a formation replacing the latters. On account both of its position corresponding to Walther's facies-rule, and of its sedimentary features respectively abundance in *Hystrichosphaeridae* and *Peridineae,* it can be regarded as sediment of a quiet, but offshore realm.

The continued subsidence of the basin is indicated by the appearance of dark-grey, thin-bedded, and even shaly, argillaceous siltstones and clay-marls (Plate V, *Fig. 1*). On the basis of its more reduced $CaCO_3$-contents and finer grain size it is really this facies that may having been deposited when the Lower Pannonian basin attained its greatest depth.

In the overlay of the clay-marl sequence, the monotonous succession of these fine-grained sediments, testifying to a steady subsidence, is followed by a varied sequence of coarser and finer sediments that alternate on very different ways. This sequence was referred to a "sandy horizon" and "sandy claymarl horizon" by L. Kőrössy [1968]. These distinctions of Kőrössy, however, are valid in rough lines only, for in a number of sections the Lower Pannonian as a whole is found to be marly including only thin sandstone intercalations. Obviously, we have to do here with facies replacing one another variedly. Their distribution has been controlled by the extension and energy and turbulence conditions of the currents of water that used to divide the coarser sediments in the more internal parts of the basin. Accordingly the manner of bedding is very variegated. In addition to laminations of varying thickness, continuous or discontinuous and parallel—horizontal (Plate V,

Fig s2—4), crossbedding of varying dip can frequently be encountered, being connected with the migrating of flatter or steeper ripples on the basin floor. The foresets of the flatter ripples have often been preserved only in the form of thin siltstone or claystone flasers (Plate VI, *Figs. 1—2*). In other case, the most different phases of the truncation and planation of the ripples can be met with. Accordingly, every sand lense embedded in a clayey or silty rock can be considered to be the remnant of a minor sand wave (see Plate VI, *Figs. 3—4*, Plate X, *Fig. 4* and Plate V, *Fig. 4* in the given succession).

Periodical increase of the turbidity of the currents can be read off those poorly sorted sandstone bands too wich are intercalated in several centi- or decimeter thickness between the parallel—horizontal or lenticular laminae (Plate V, *Fig. 4*, Plate VI, *Fig. 1* and *3*; Plate VIII, *Figs. 1—2*). In accordance with this phenomenon these sandstone sections frequently abound in silt(stone) or clay(stone) pebbles undoubtedly underwent transportation (Plate VII, *Fig. 2*, bottom; Plate VIII, *Figs. 1—2*, top; Plate IX, *Fig. 5*).

The rectilinear grading of some sandstone bands (Plate VI, *Fig. 4*, lower part), however, indicate the turbidity current to have gradually decreased in energy.

As a result of the combination of the afore-mentioned types a composite bedding has developed in many cases (Plate VI, *Fig. 4*; Plate X, *Fig. 4*).

Differential load due to sand waves thicker in the centre has brought about load casts and compensating flame structures in the fine mud that was originally still filled with water (Plate VI, *Figs. 3—4*). In consequence of the sinking of the primarly emerging (positive) forms into the mud, the differential load produced diversified convolutions of the foresets (Plate IX, *Fig. 1*). This kind of sedimentary deformation, however, often occurs even in cases when no trace of sand wave formation is available (Plate V, *Fig. 3*; Plate VII, *Figs. 1—3*; Plate VIII, *Figs. 1—2*). In such cases one has to think the freshly deposited sediment to have been shaken (e. g. as a result of an earthquake due to the subsidence of the sedimentary basin).

Folds (Plate IX, *Fig. 2*) due to subaquatic slumping and sliding respectively faults (Plate IX, *Fig. 3*) due to foundering of the sediment also occur frequently in the Lower Pannonian sequence. The resultant convolution structures (Plate X, *Fig. 4*, bottom) cannot always be distinguished sharply from the convolutions due to differential load (see also Plate VIII, *Figs. 3—4*).

On account of the close interconnection between their occurings, the silt(stone) and clay(stone) pebbles, so frequent in the sandy members of the Lower Pannonian and often showing up proper internal structures (Plate IX, *Figs. 4—5*; Plate X, *Figs. 1—2*), should be supposed to have been in genetical connection with slumpings due to synsedimentary tectonism. Unlike usually believed, we do not think that these might be inferred from mud curls or flakes formed by desiccation during ebbs or, in general, at low water stage. The present writer believes that — at least in this case — sediment-fragments of partly already consolidated state torn away by subaqueous slumping and these were brought to site of their deposition by water current suddenly accelerated by the slumping itself. This is evidenced by the fact that they can always be found within coarser sediments whose appearance can be referred to strong water currents. Of course, it is possible that subaqueous slumping is a polygenetic phenomenon wich can be provoked also by changes in the direction or intensity of primary water current. The formation and transport of the silt(stone) pebbles, however, must be regarded by all means as a consequence of slumping.

The most direct marks of the resultant currents, however, are represented by flute casts (Plate X, *Fig. 3*). Even though occasionally load-casted, the furrows and fillings of these can be readily recognized in most of the cases.

All these sedimentary features of the Lower Pannonian of the southern Great Hungarian Plain seem to be absent in the marginal sequences of the same age. The similarity of these features to those of the marine Tortorian sediments uncovered in the same region indicates that the two transgressions must have had the same mechanism with currents formed under conditions of subequal depth and bottom relief.

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EXPLANATION OF THE PLATES I—X

PLATE I

1. Coarse, massive, poorly sorted coastal conglomerate consisting of pebbles of crystalline schists. — Lower part of the Tortonian basal conglomerate complex. — Well Dorozsma-4. 2937,30—2937,44 m. Side-view.

2. Coarse, massive, poorly sorted, polymict breccia composed prevailing of fragments of Triassic rocks. — Lower part of the Tortonian basal conglomerate complex. — Well Szeged-7. 2828,71—2829,00 m. Polished surface.

3—4. Mesh-like eddy structures formed by horizontal vortices. — Middle part of the Tortonian basal conglomerate complex. — Well Szeged-2. 2666,00—2679,50 m. Side-view.

Plate II

1. Outwash and mesh-like eddy structures from the middle part of the Tortonian basal conglomerate complex, on the contact of lenses of fine-grained dolomite-conglomerate and coarse dolomite—quartz sandstone. — Well Szeged-2. 2666,00—2679,50 m. Polished surface.

2. Mesh-like eddy structures formed by small dolomite pebbles, in the faintly calcareous dolomite — quartz sandstone of the middle part of the Tortonian basal conglomerate complex. — Well Szeged-2. 2666,00—2679,50 m. Polished surface.

3. Poorly sorted, medium-grained dolomite-sandstone with lenses of dolomite-pebbles. — Upper part of the Tortonian basal conglomerate complex. — Well Szeged-7. 2788,90—2789,12 m. Polished surface.

4. Four directly sorted small rhythm from the upper part of the Tortonian basal conglomerate complex. — Well Szeged-7. 2780,35—2780,60 m. Polished surface.

Plate III

1. Parallel—horizontal lamination in the fine-sandy and silty marl beds of the Tortonian marl complex, with pyrite lenses seeming on the picture to be white. — Well Szeged-2. 2656,00—2665,00 m. Polished surface.

2. Folding in the dark-grey and black, discontinuous-horizontal laminae of the Tortonian marl complex suggesting mud flow. — Well Szeged-2. 2656,00—2665,00 m. Polished surface.

3. Folding deformation caused by submarine slumping of the originally parallel-horizontal laminae of the black argillaceous siltstone and light-grey, fine-grained sandstone in the somewhat higher part of the Tortonian complex. — Well Hódmezővásárhely-1. 5654,00—5654,30 m. Side-view.

4. Coarse, massive, poorly sorted conglomerate from the lower part of the Lower Pannonian basal conglomerate complex consisting of pebbles of crystalline schists. — Well Algyő-91. 2535,82—2536,09 m. Side-view.

Plate IV

1. Massive, poorly sorted, coarse sandstone with small pebbles. — Higher part of the Lower Pannonian basal conglomerate complex. — Well Algyő-50. 2500,00—2500,92 m. Side-view.

2. Mesh-like eddy structures formed by the stir up of the deposited sediment in a coarser intercalation of a fine-grained sandstone. — Top of the basal conglomerate complex of the Lower Pannonian. — Well Algyő-248. 2724,06—2724,25 m. Side-view.

3. „Cloud-like transition" between stripes of the fine-sandy calcareous siltstone and the interbedded coarse sandstone formed by the stir up of the deposited sediment. — Direct cover of the Lower Pannonian basal conglomerate complex. — Well Algyő-85. 2864, 97—2865,17 m. Side-view.

4. Discontinuous-horizontal lamination: above coarser, below finer-grainded laminae of marl in the marl complex of the Lower Pannonian. — Well Szeged-2. 2593,18—2593,58 m. Polished surface.

Plate V

1. Dark-grey, thin-bedded, fissil argillaceous siltstone. — Higher part of the Lower Pannonian. — Well Algyő-82. 2489,35—2489,57 m. Side-view.

2—3. Dark-grey, calcareous siltstone, with horizontal-parallel laminae of a light sandstone. On the bottom surface of some of the thicker sandstone-laminae small load pockets and flame structures. — Higher part of the Lower Pannonian. — Well Szeged-9. 2528,55—2228.70 m. Side-view.

4. *Below:* Dark-grey siltstone, interbedded with thin, horizontal-parallel bands and lenses of sandstone. *Above:* Covering the formers, light-grey, massive, fine- and small-grained calcareous sandstone with muscovite flakes. — Higher part of the Lower Pannonian. — Well Szeged-9. 2714,69—2714,87 m. Side-view.

Plate VI

1. Flaser-structure in a small-grained sandstone interbedded with argillaceous marl. — Higher part of the Lower Pannonian. — Well Ferencszállás-13. 2508,32—2508,70 m. Side-view.
2. Siltstone-flasers among ripples of a light-grey, fine- and small-grained sandstone having a flate cross-bedding. — Higher part of the Lower Pannonian. — Well Ferencszállás-6. 2260,50—2260,65 m. Side view.
3. Cross-bedded ripple intercalated between horizontal-parallel beds. — Higher part of the Lower Pannonian. — Well Szeged-7. 2335,30—2335,43. Side-view.
4. Development of a discontinuous, lense-like structure formed both by sunk and planed, cross-bedded ripples, from a horizontal-parallel laminated sandstone. The thick lense in the upper part of the picture represents a sunk ripple. — Higher part of the Lower Pannonian. — Well-Szeged- 9. 2467,66—2467,85 m. Side-view.

Plate VII

1. Contact between a grey siltstone and a fine- and small-grained sandstone band, with load marks and compensating flames. — Higher part of the Lower Pannonian. — Well Algyő-82. 2485,22—2485,30 m. Side-view.
2. Large load marks of a lighter-grey, coarse sandstone sunk into a fine -grained sandstone with siltstone lenses. — Higher part of the Lower Pannonian. — Well Algyő-82. 2486,12—2486,21 m. Side-view.
3. The plane of the fine-grained sandstone pictured on the Fig. 2., with moulds of load pockets.

Plate VIII

1—2. Flame-structures in a sandstone, that alternates below with thin siltstone-stringers, but includes above siltstone-pebbles. — Higher part of the Lower Pannonian. — Well Szeged-2. 2416,93—2417,16. m. Side-view.

3—4. Dark clay marl with sunken parts of the covering fine-grained sandstone, partly dissected by mud-flasers. — Higher part of the Lower Pannonian. — Well Ferencszállás-13. 2390,85—2391,05 m. Side-view.

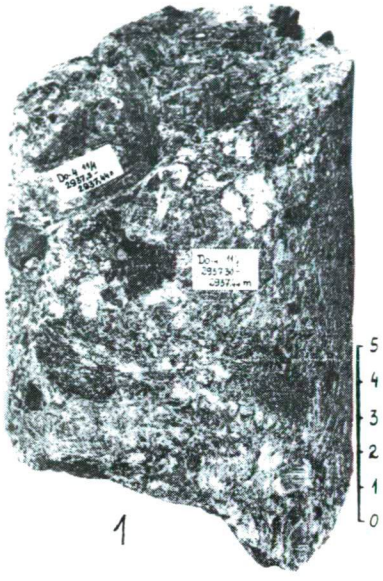
Plate IX

1. Convolution of sand waves sunken by differential load into the underlaying siltstone. — Upper Pannonian. — Well Algyő-242. 1965. m. Side-view.
2. Folding caused by sub-aqueous slumping in alternation of fine- and coarse-grained siltstone-laminae with that of fine- and small-grained sandstone. — Higher part of the Lower Pannonian. — Well Ferencszállás- 13. 2214,31—2214,62 m. Polished surface.
3. Minor sedimentary fault crossing horizontal-parallel laminae of sandstone interbedded with argillaceous siltstone. — Higher part of the Lower Pannonian. — Well Algyő-86. 2422,50—2422,84 m. Side-view.
4. Biscuits of fine-grained siltstone with proper lamination, embedded in a poorly sorted, coarse- and fine-grained sandstone. — Higher part of the Lower Pannonian. — Well Szeged-9. 2465,40—2466,40 m. Polished surface.

5. Minor siltstone pebbles and current ripple foreset-bedding in a poorly sorted sandstone. — Higher part of the Lower Pannonian. — Well Szeged- 9. 2465,10—2465,40 m. Side-wiev

PLATE X

1. Biscuits and bits of fine siltsone with proper lamination embedded in a poorly sorted, fine-grained sandstone. — Higher part of the Lower Pannonian. — Well Szeged-9. 2465,60—2465,78 m. Polished surface.
2. A sample from the higher part of the Lower Pannonian attesting the sudden change of the current conditions. Below and at centre: parallel-horizontal bedding proving a stillwater-sedimentation. In the middle of the lower part convolute ripples, on top of the specimen siltstone-pebbles embedded into sandstone. — Well Algyő -264. 2410,65—2410,80 m. Side-view.
3. Filling-up of flute marks on the bottom surface of a fine-grained sandstone bed stepping over to fissil siltstone. — Higher part of the Lower Pannonian. — Well Algyő-83. 2485,93—2485,98 m. Side-view.
4. Composite bedding in higher part of the Lower Pannonian strata. Below laminae of sandstone and siltstone suffered convolution by mud flow. Higher eroded ripples with foreset-bedding. In the middle massive, fine-grained sandstone with small load pockets on the bottom surface. Over this sandstone band planed sand ripples, inside the overlaying siltstone, however, parallel-horizontal sandstone lenses and laminae. In the sandstone lenses oblique or perpendicular tubes of burrowing organisms. — Well Szeged-9. 2714,74—2718,15 m. Side-view.



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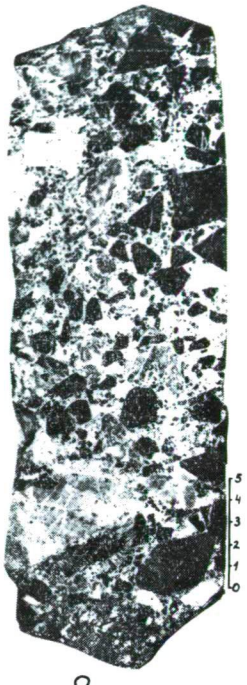

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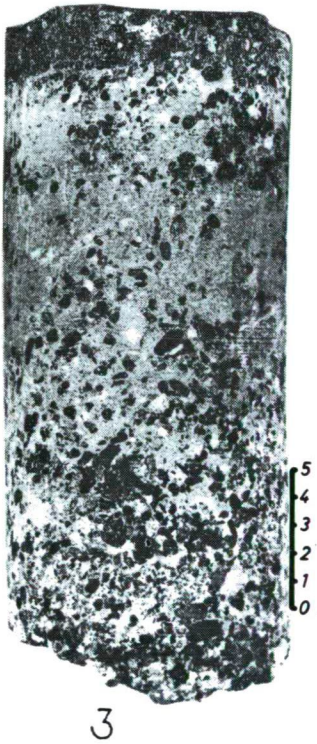

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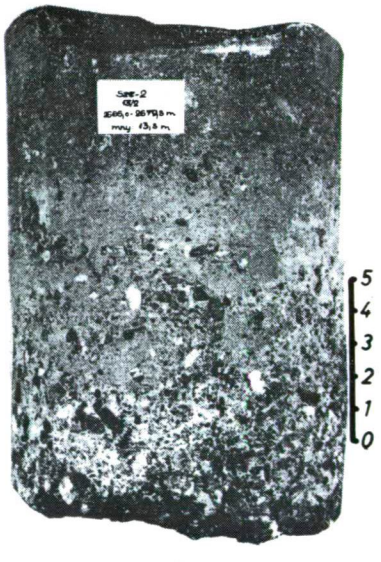

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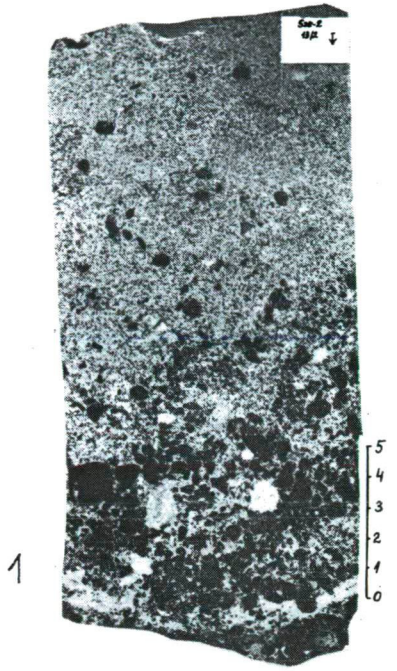

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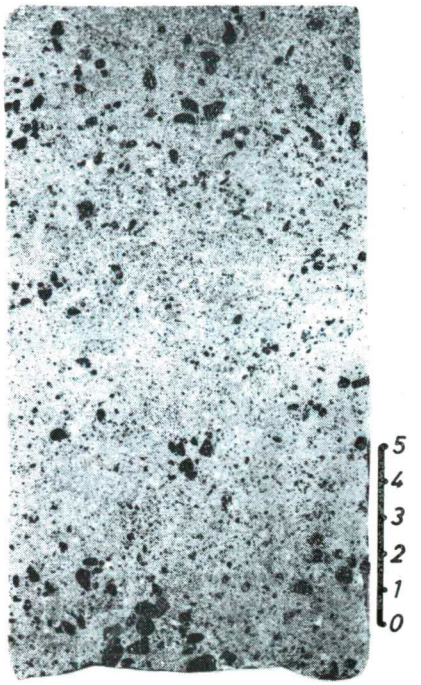

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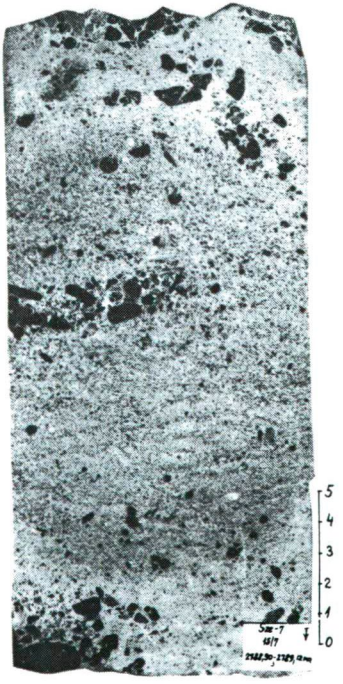

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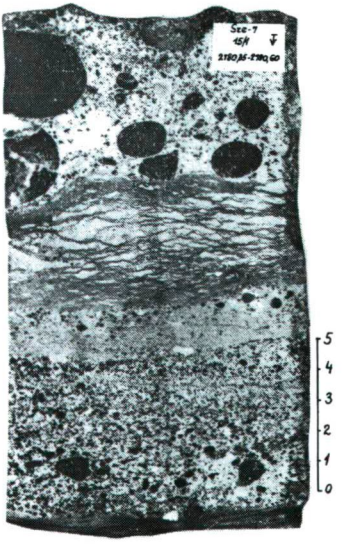

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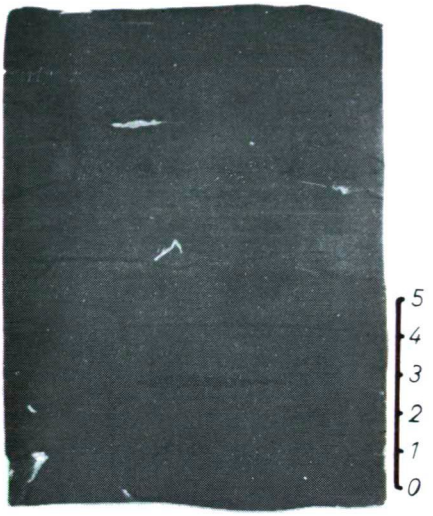

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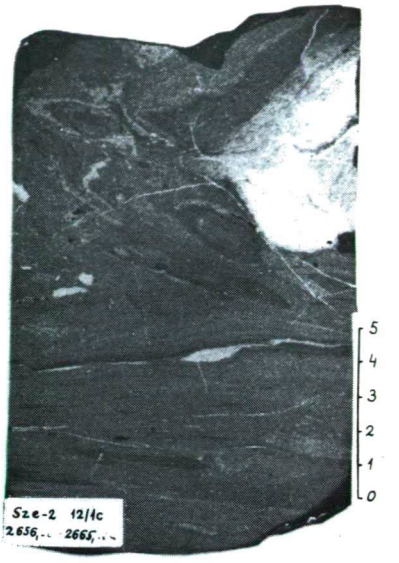

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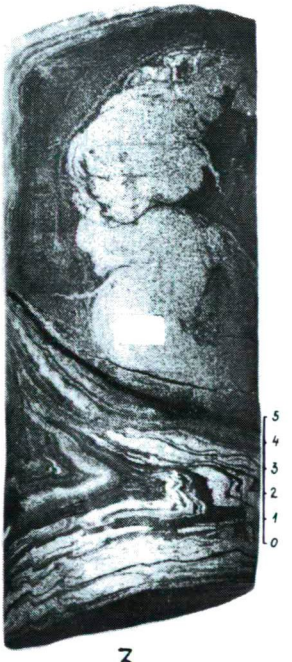

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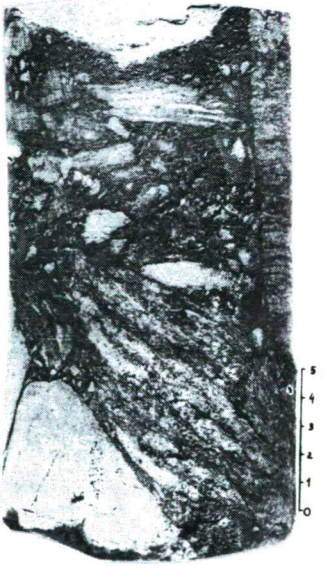

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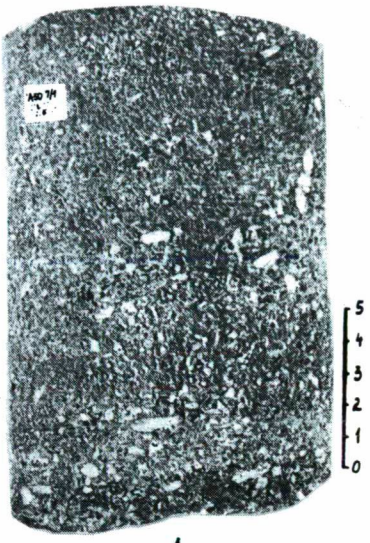

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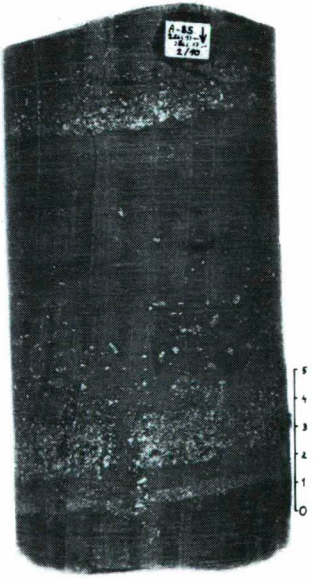

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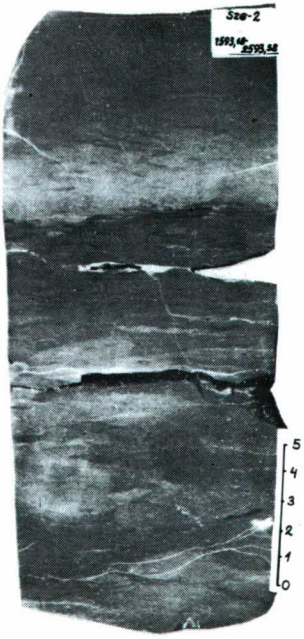

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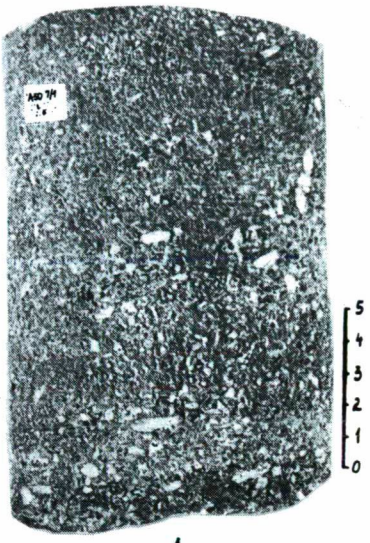

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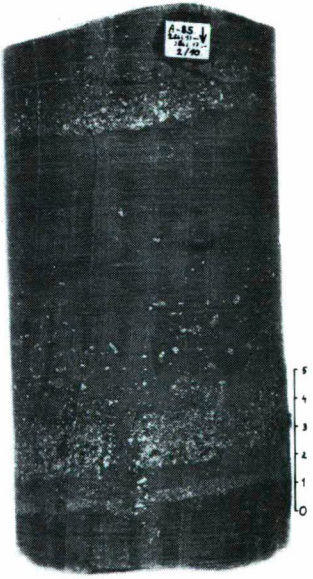

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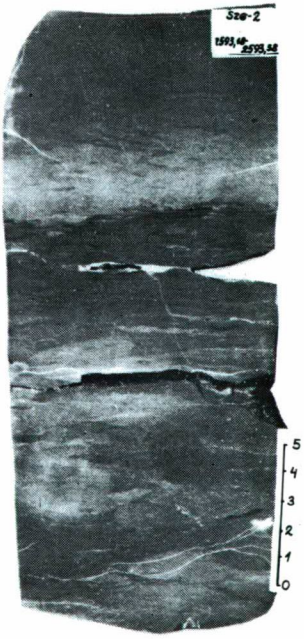

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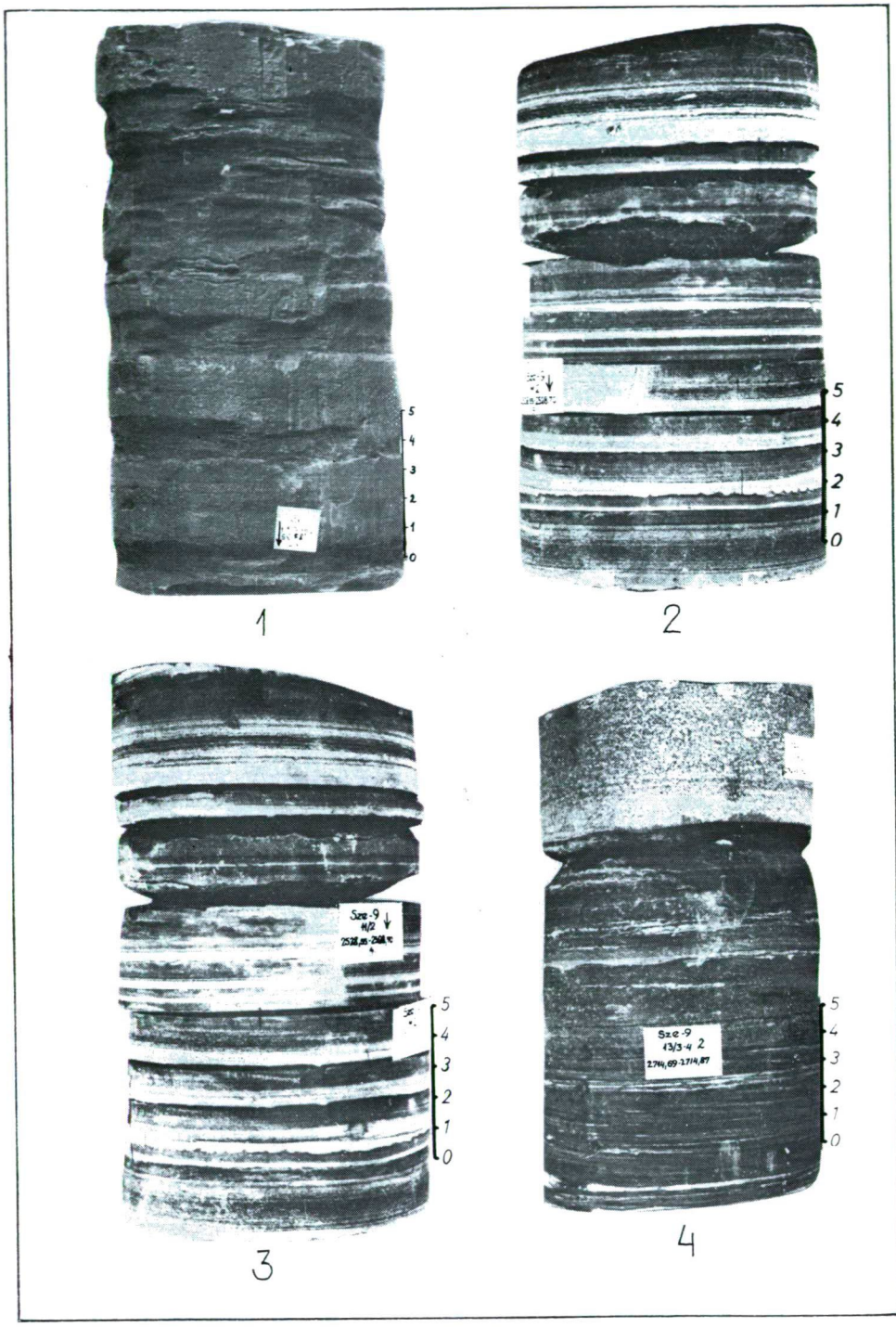
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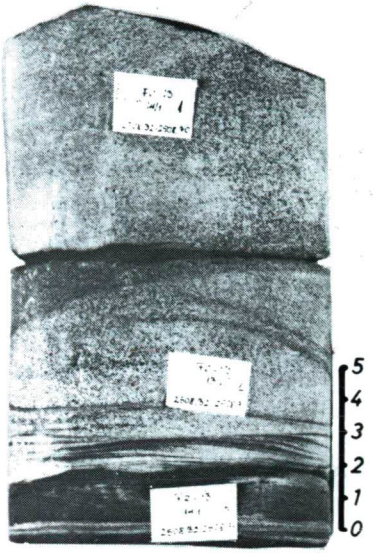

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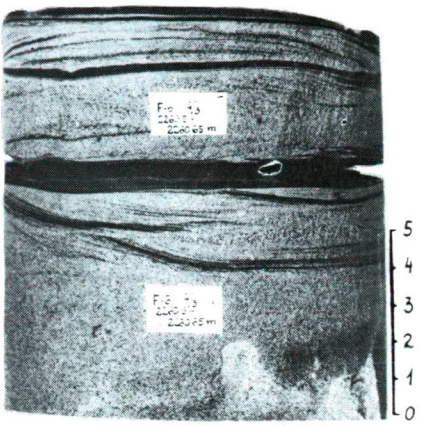

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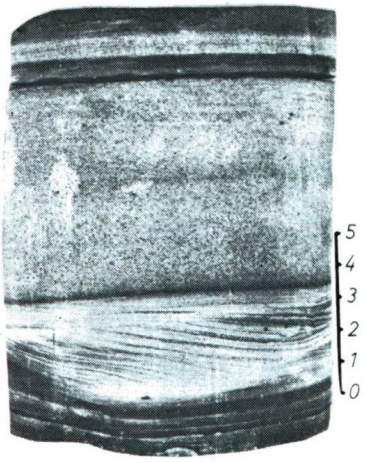

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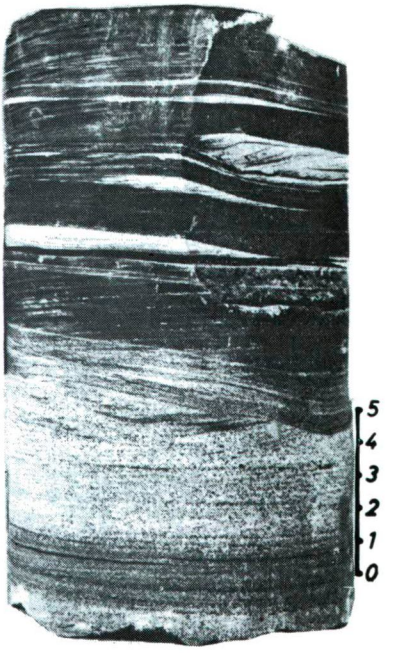

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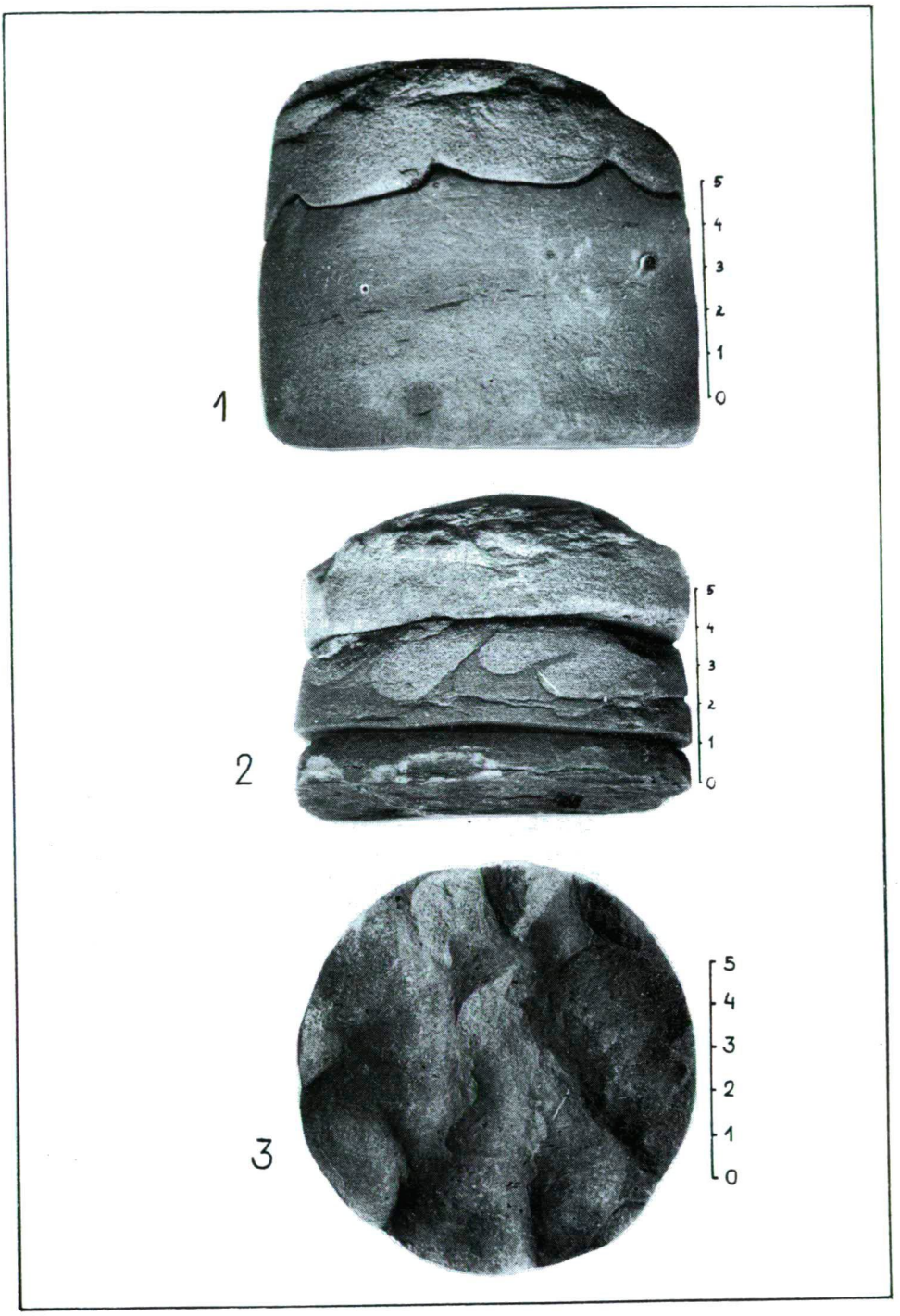
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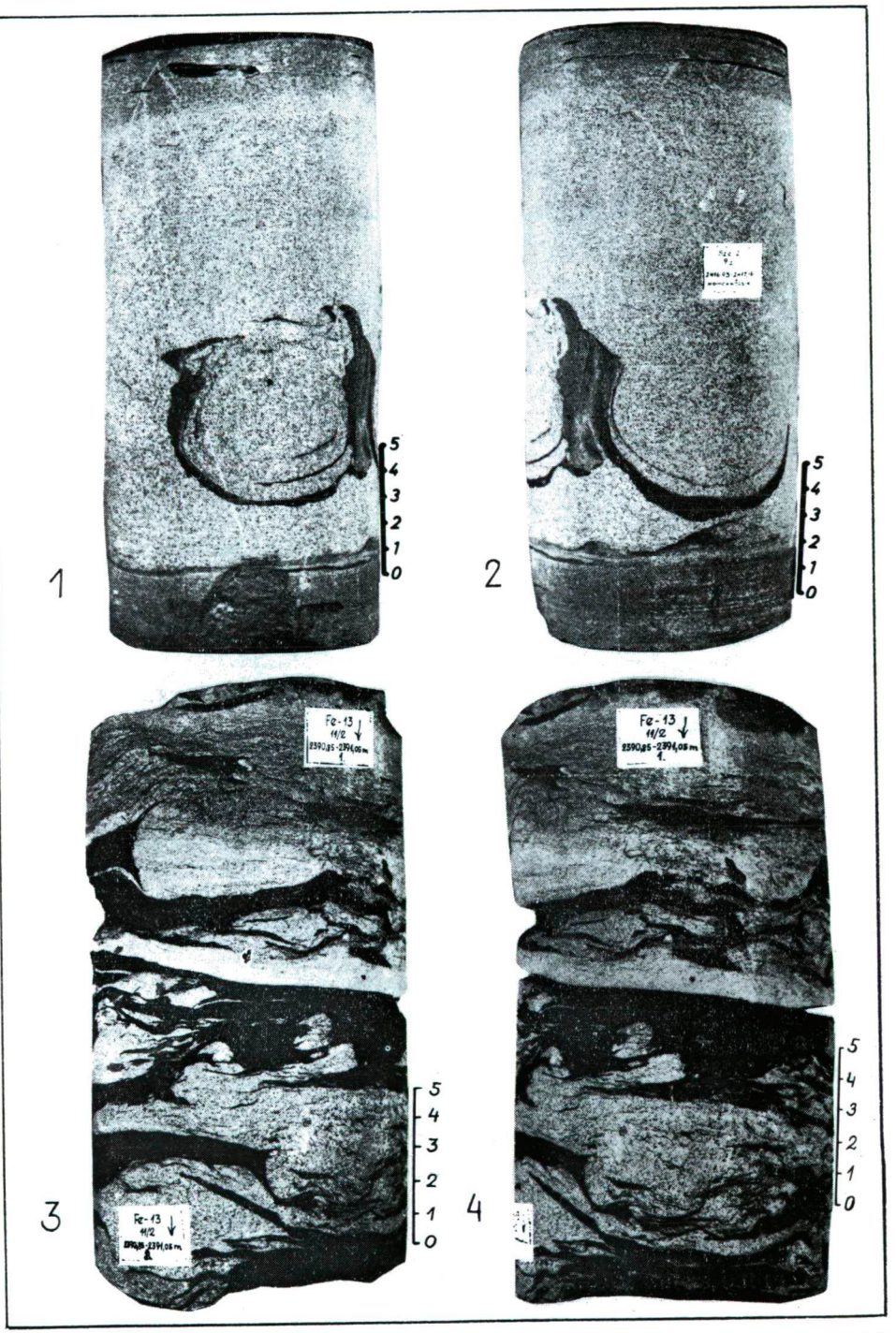
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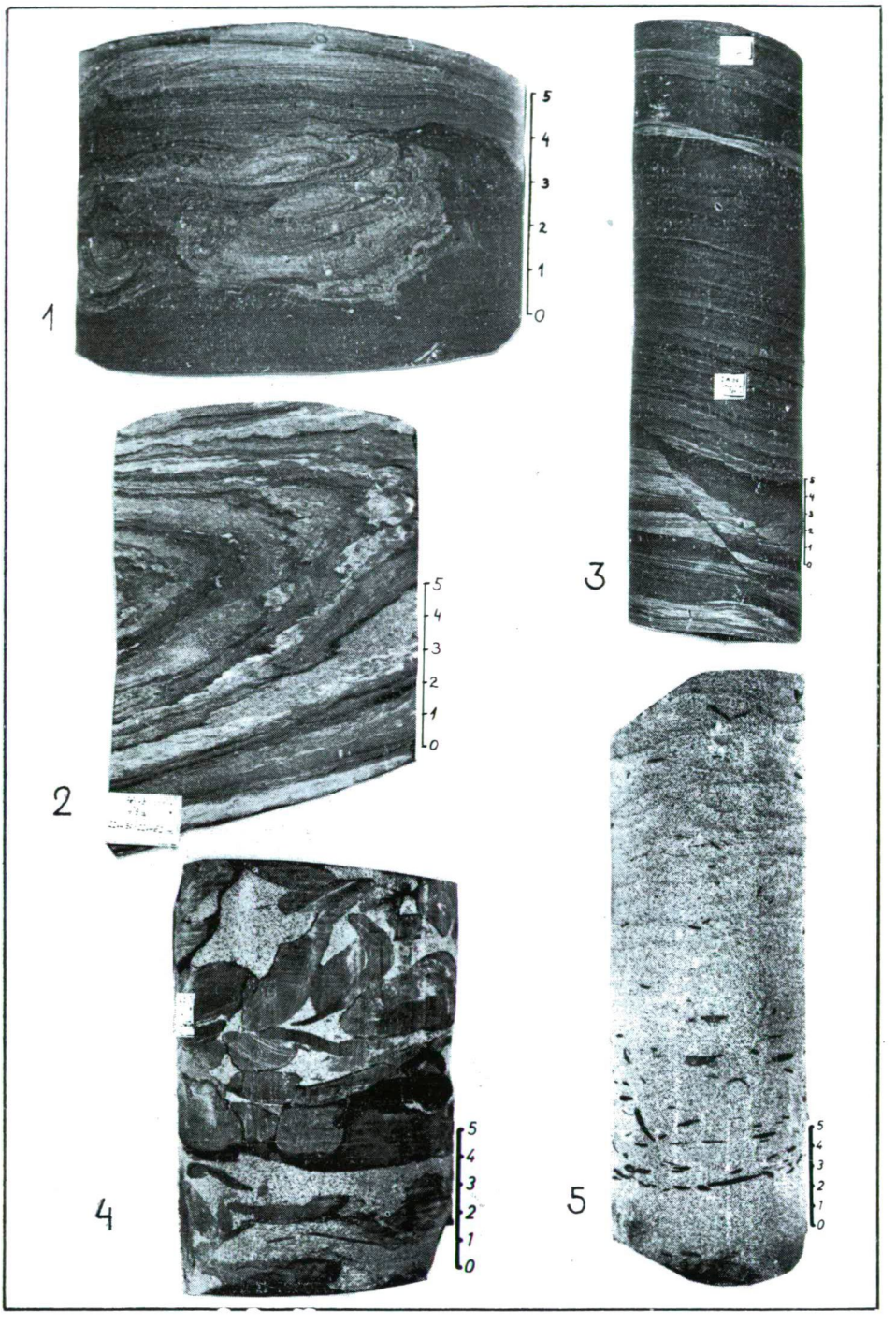
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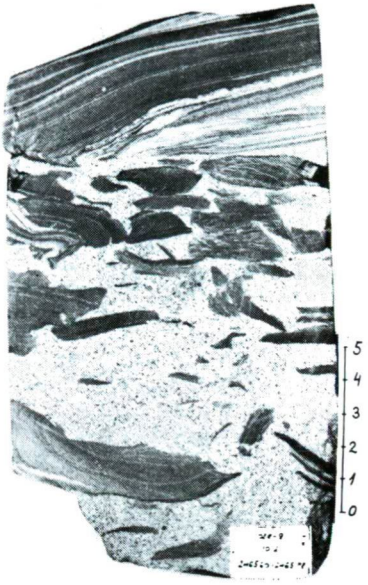

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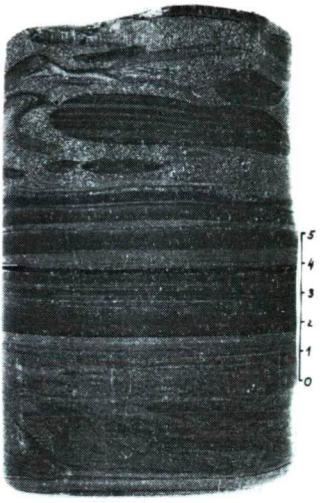

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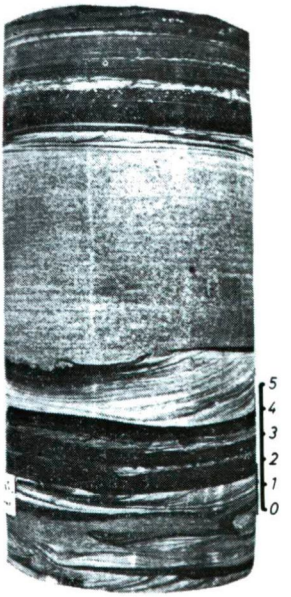

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Acta Mineralogica-Petrographica, Szeged XXI/1, 41—47, 1973

MINERALOGICAL-PETROGRAPHICAL AND CHEMICAL INVESTIGATION ON ARCHAEOLOGICAL CERAMIC GRAVEGOODS

GY. DUMA and CS. RAVASZ

As well known, an important part of the archaeological finds consists of utensils, vessels or building material made of fired clay. It can be easily understood that the claim to study this material, often very important from an archaeological point of view, with modern scientific methods, necessarily arose recently all over the world.

With the spreading of the scientific methods of approach, it was natural to realize the fact that the results of the modern testing may be a great help in archaeological identification of finds. It becomes clear, however, that in the investigations on archaeological material numerous particularities have to be taken into consideration, which cause the methods developed and generally used to give results to insufficient in some cases.

The difficulties in determination of ceramic products arrive partly from the processing, partly from the physical and chemical effects of being buried in the earth, and which may alter the original state, the natural composition and structure of the clay, in a not negligible measure. The sluicing of the clays used for pottery, their mixing with further mineral substances — lean material — leads to changes in the natural ratio of the mineral constituents; their forming and throwing (working on the potter's wheel) causes of the texture, finally the firing produces chemical and physical changes, considerably modify the mineral composition. As in the most cases it is impossible to distinguish the changes caused by human activity from those due to natural circumstances, in our investigations to be described, we used the antropogene effect, too, as characteristics and criteria for determining identities or differences.

Investigations for archaeological purposes were made on ceramics material from the beginning of our century and even earlier. As in those times chemistry was in the foreground among of natural sciences, it is easy to understand that, chemical methods were employed for determining ceramics. However, as in consequence of their structure, both the raw material of ceramics and, the end-products can be characterized, only by the chemical components, the determinations based solely on the results of chemical analysis cannot be satisfactory, except special cases.

It follows from the character of the ceramic material, that the scientific determination of both the raw material, and the end-products can be based, in the first line, on their mineral constituents. It can be understood, that in our days the methods — for mineralogical-petrographical determinations — chiefly thin slides — are often used for characterizing ceramic finds. Thus for studying ceramics made from

potter's clay it was necessary to elaborate methods, in which spite of difficulties the results of chemical analyses and petrographical determinations assert themselves, and their simultaneous evaluation becomes possible.

Therefore it has been tried to draw inferencies, concerning the minerals constituting the raw materials, calculations based on the analytical data of the chemical components, in order to divide into groups the material of ceramic finds.

The calculation generally used in silicate-chemistry, do not give, however, satisfactory results in the case of potter's clays, due to the presence of different clay minerals pertaining to the montmorillonite and mica group, which are hardly to be characterized chemically. As the silicates (except some alkali-silicates) can be decomposed only by fusion, the result of chemical investigations will not be able to answer the questions concerning the original connections between the components, the composition of minerals. This logically leads to our earlier statement, that the pottery, row, and fired products alike, the chemical composition in itself cannot be characteristic.

TABLE 1

Chemical analyses (weight percent) of the ceramics Szekszárd—Palánk find

Sample	Group	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ing. loss.
39	A	75,1	9,8	7,1	1,5	0,8	1,5	0,5	3,2
40		73,8	9,9	7,0	1,9	0,6	1,5	0,5	4,5
28	B	46,1	13,9	8,9	11,2	3,0	2,9	0,4	13,2
29		48,4	15,5	9,2	11,5	3,5	2,9	0,6	8,0
30		58,8	18,0	9,5	3,8	3,0	2,4	0,3	4,0
31		54,6	16,6	9,5	7,2	4,9	2,4	0,4	4,1
34		46,1	13,0	9,7	9,8	4,2	2,8	0,3	13,8
38		53,8	17,2	10,3	2,6	3,6	2,9	0,4	8,8
41		48,4	15,8	8,9	9,9	4,4	3,1	0,5	8,6
44		47,0	13,6	7,8	12,6	2,8	3,1	0,4	12,5
45		54,7	16,7	8,7	7,2	3,5	3,7	0,5	4,7
47		50,6	15,8	9,1	10,1	3, 3	3,6	0,3	6,8
50		51,4	15,1	12,0	7,0	3,5	4,0	0,4	6,4
51		53,3	15,9	9,3	8,6	4,0	3,9	0,5	4,0
52		45,9	14,6	8,2	10,2	4,0	3,7	0,2	13,0
54		49,6	14,8	10,4	6,6	2,0	2,9	0,3	11,8
55	C	44,9	13,5	7,7	13,1	3,1	3,9	0,4	12,9
37		65,8	12,6	8,5	2,0	1,6	1,3	0,6	7,2
46		73,3	14,7	5,9	1,1	0,9	0,9	0,4	2,6
49		66,6	11,9	8,9	2,3	1,6	2,0	1,0	5,1
53		69,0	15,3	6,7	1,6	0,9	0,8	0,3	5,1
27	D	67,1	16,0	10,1	1,4	1,7	1,4	0,4	1,6
33		38,4	8,2	5,4	21,6	2,4	1,6	0,4	21,5
35		56,2	13,7	8,9	5,0	4,2	2,0	0,3	9,4
36		51,2	11,9	10,6	7,9	4,2	3,8	0,4	9,6
42		54,5	13,2	9,2	9,2	3,5	3,1	0,5	6,5
43		59,4	15,0	9,7	6,3	2,8	2,4	0,4	3,5
32	B/D	51,9	13,5	8,7	10,6	3,6	3,1	0,5	7,5
48		52,4	14,4	9,0	5,8	4,7	2,4	0,2	10,6

As known, in the clays processes connected with the loss of weight occur during the firing. This loss of weight manifests in the loss an ignition, and therefore it is always an important and characteristic factor among the components, resulting from chemical analysis. The fired clay — pottery — will show further ignition losses only in the case, if the thermal modifications, connected with loss of weight, have not been terminated during the firing, or the material of the pottery suffered changes after the firing, which subsequently may produce such processes. We found that the refiring of the material of unglazed pottery, produced with primitive technology, and buried in the earth mostly results in significant loss of weight. In the fragments exposed during the excavations we often could observed the enrichment in organic and various inorganic material; in several cases also some transformation, rehydration of the clay minerals could be determined. As the value of the ignition losses of the pottery and end-product is significantly modified by all these processes, therefore the losses in weight of the ceramic material of excavation, caused by firing cannot be considered as characteristic, neither for the original pottery, nor for its raw material.

It follows from the above that ceramics can be compared with mutually on the base of their components if they do not show any loss on ignition, or of the losses found represent their full value. The first condition practically applies only to compact, non porous pottery, the second only on the state preceding firing. The ignition losses found in all intermediary states introduces uncertainties in the evaluation of the comparative studies. In the material investigated by us the ignition losses varied between 1,6 and 21,5 weight percent (Table 1).

Owing to the above, it is not possible to compare the ceramics, brought to light during the excavations, directly on the base of quantity of their chemical components. Therefore our calculations were made on the basis of the relative distribution of components can be taken into consideration, which may be characteristic both for the raw material processed and for the ceramic product. Generally three components are chosen; for comparing the relative quantity of the latter, the method generally used for the representation of three-component systems, proved to be very suitable.

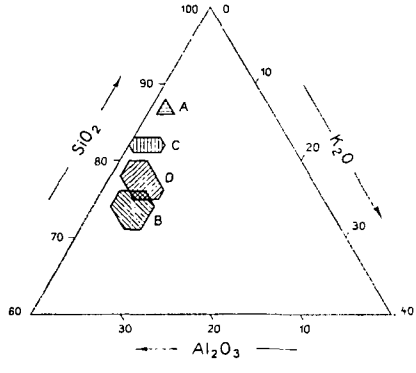


Fig. 1. Arrangement of the main sample-groups formed by the comparison of the chemical and petrographical data, in the SiO_2-Al_2O_3—K_2O system.

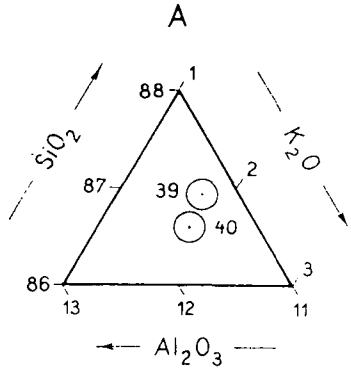


Fig. 2. The samples of the A-group plotted in the SiO_2—Al_2O_3—K_2O ternary system.

We found in many cases, that — similarly to example given in *Fig. 1* — the ceramics could be characterized by the percentual distribution of three components Al_2O_3—SiO_2—K_2O.

This choise cannot be considered as generally valid, because it is characteristic only for certain type of clay. It is, however, in good agreement with our finding, that in the Pannonian pottery's clays the dominant clay minerals are mostly hydromica and illite. In some cases we used the K_2O+Na_2O content; or the some of several components to calculate the relative value.

The mineralogical and petrographical studies on the ceramics were made with the petrographical thin slide methods generally used. Similarly as for rocks, this method permits to determine the mineral composition, the quantity of the constituents of the sample, as well as of their shape, dimensions, and mutual spatial arrangement (texture). As the our methods used in those investigations are of petrographic character: in our opinion the ceramics are to be considered as rock, despite of the antropogene effects mentioned above. Therefore in our descriptions we used the petrographical nomenclature in all cases.

The comparison and grouping of the data of macroscopic and microscopic examinations, based on similar features is not necessarily limited to statistical identification of the characteristics mentioned, as the raw material of the samples studied originates from fragmentation of earlier rocks. One of our further target may be the determination or reconstruction of the original locality of these rocks. In our work, depending on the number and character of available data, we tried to give an answer to these questions of genetic character, too.

In the following, we wish to exemplify the method described above, which is one of the possibilities evaluating the combined result of quantitive chemical analyses and mineralogical-petrographical studies by our investigations, on the material of the VI—VII Century Avar cemetery in Szekszárd-Palánk (SW-Hungary) excavated between 1958—1962.

The raw material of the samples, in its geological sense, was clay, sandy clay and calcareous sandy clay. The separation of the main groups was made on the basis of the different ratio of the contents in calcareous material, SiO_2, and clastic minerals.

I. Sandy clay: sedimentary rock formed in seawater. Detailed evidence concerning its geological age is not available. The matrix consists mostly of recrystallized — partly of amorphous — SiO_2 network, containing sericite of laminar texture, altered biotite, more rarely of carbonate patches.

The material of the clastic minerals is: quartz (chiefly of magmatic origin) potash-feldspar, biotite, limonite, some plagioclase. In some samples haematite can be recognized.

Fossil debris of limy material are seldom. The samples No. 28, 32, 34, 47, 48, and 51 can be classed in the group.

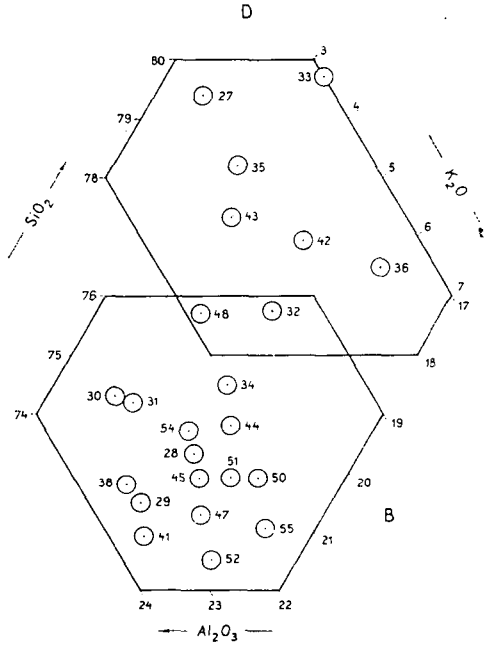
II. Silty clay, with patches of calcareous material. The material of this group originates from overwhelmed volcanic rocks, the mineral composition points to Miocene volcanic products. The samples can be divided into several subgroups, based on qualitative and quantitative differences in clastic minerals.

a) Much amorphous or recrystallized SiO_2, and much biotite as matrix with very little fine-sand. The latter consists of quartz, limonite, some plagioclase, and a few tiny zircon and apatite crystals. Samples No. 36, 41, 42, 45, and 50 belong to the subgroup.

b) In a matrix of SiO_2, biotite and little calcareous material, detritus of silt and sand sized. The SiO_2 in the matrix is amorphous or recrystallized: as a clastic component appears in the form of quartz. Greater quantities of muscovite and feldspar are to be mentioned, too. Heavy minerals: magnetite, limonite, garnet, apatite, sphene, some hypersthene crystal fragments. This subgroup includes the samples No. 29, 35, 38, 44, 52, 54 and 55.

c) More clayey, of lesser siliceous character than the precedent subgroup. The bulk of the clastic minerals consits of quartz, plagioclase, potash-feldspar, biotite, limonite, chlorite, and muscovite. Heavy minerals: zircon, rounded rutile and sphene. The samples No. 30, 31, 33, and 44 are to be reckoned to the subgroup.

III. This group consists of the most heterogeneous material: the clastic material originating from erosion of volcanic, plutonic and metamorphic rocks, enclosed in a clayey matrix. Oligocene age of formation is rendered probably by mineralogical, petrographical analogy. The subgroups are based chiefly on differences in the texture of the rock or caused by firing.



Fig, 3. The samples of the B and D-groups in the SiO_2—Al_2O_3—K_2O ternary system.

a) Siliceous-clayey matrix with much silt and fine grained sand. The material of the clastic components is quartz, orthoclase, muscovite. Heavy minerals: ironhydroxides, and a some epidote, apatite, hypersthene, rutile, sphene, tourmaline, zircon, magnetite, kyanite. Samples No. 46 and 47 can be ranged with this subgroup.

b) Red, clayley matrix coloured by ironhydroxide, much silt, with clastic material of fine and medium grained sand. Clastic minerals: quartz in the bulk (both magmatic and metamorphic), partly altered feldspar (potash-feldspar and acidic

plagioclase), muscovite, chlorite. Heavy minerals: zircon, apatite, biotite, tourmaline, epidote, magnetite, hypersthene, kyanite and garnet. As rock fragments some quartzite, and limestone of fine crystalline texture containing magmatic quartz, occur sporadically. Samples No. 37, 39, 40, 49 belong to the subgroup.

c) Sandy clay. Only one sample, the coarser, the medium grained clastic material and the angular grain contours of which are different from all other samples. The most of the clastic minerals are quartz, the major part of which is of magmatic origin, a minor part being metamorphic. Heavy minerals:sphene, chlorite,hypersthene, apatite, zircon, rutile. As rock fragment a single grain of sandy marl can be recognized. This subgroup is represented by sample No. 53.

As can be seen from the above, it is possible to make comparatively very fine distinctions on the basis of mineralogical-petrographical macroscopical and microscopical investigations within the ceramic material of an archaeological excavation. Further refinements are possible with the aid of micromineralogical studies, and, in the first line by X-ray investigations for the qualitative determination of the clay-minerals and SiO_2 varieties. This possibility was already used by the authors in investigations on the material of an other find, result of which will be presented elsewhere. The authors come to the conclusion that, though further differentiations are possible compared with the results of study based only on thin slides and the conclusions can be supported by further data; but the identities of differences cannot be easily recognized by the archaeologist on the ceramics itself, these studies do not help immediately in approaching the purpose. It should be mentioned, further, that the petrographical features cannot be served as primary, determinent characteristics for the archaeologist, because other points of view, discussed in the introduction have also to be taken into consideration.

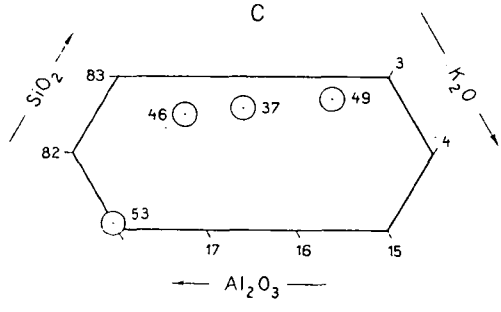


Fig. 4. The samples of the C-group in the SiO_2—Al_2O_3—K_2O ternary system.

The three-component representation based on chemical analysis by generalizing the petrographical features in a certain degree, proves to be very usefull in presenting or confirming the similar results of chemical and petrographical investigations *(Fig. 1, 2, 3, 4)*. This principle and method of grouping is proved to be very suitable in our practice for drawing conclusions, which are in accordance with the results of archaeologist. It is obvious that the number of the samples exerts a substantial influence on the value of scientific investigation. Reliable result based on few samples can be expected only in exceptionally cases.

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PERONIDELLA BALOGHI, A NEW INOZOA FROM THE UPPER PERMIAN OF THE BÜKK-MOUNTAINS (HUNGARY)

HELMUT W. FLÜGEL

INTRODUCTION

The Upper Permian of the Bükk-Mountains was last described by K. BALOGH [1964]. In his monography of this region, the description of the Permian was based on the determination of the brachiopoda by Z. SCHRÉTER [1963] and of the algae by M. HERAK & KOCHANSKY, V. [1963]. In 1944 F. HERITSCH described some Permian corals from this region but most of his determinations are incorrect [H. FLÜGEL, 1970].

For stratigraphical studies the most important profiles are the outcrops in the railway-cuts near Nagyvisnyó. During a short visit to these localities the writer found specimens of a new Inozoa in a bed situated a few meters over the "Lyttonia-bank" of the Upper Permian. Descriptions of sponges from that stratigraphic horizon are rare.

COLLECTING LOCALITY

The sponges were obtained from the railway-cut Nr. 5, 2 km northeast of Nagyvisnyó near railway-point 435 [K. BALOGH, 1964. p. 596]. The profile at this point is to divide in two parts that are separated by a limestone-bank with *Leptodus (=Lyttonia) nobilis* WAAGEN. The lower part consists of dark-grey limestone-beds with algae, foraminifera, bryozoa, molluscs and crinoids. The upper part is maked of black and grey marls alternating with thin beds of limestone containing a large brachiopod-faune (="beds with Lyttonia" in BALOGH, 1964). The sponges occur cca 3 m over the Lyttonia-bank within a biomicritic limestone.

PALAEONTOLOGICAL DESCRIPTION

CALCISPONGEA

ORDO: *Pharetronida* ZITTEL

SUBORDO: *Inozoa* STEINMANN

Fam.: *Elasmostomatidae* DE LAUBENFELS 1955

GENUS: *Peronidella* HINDE 1893

Peronidella baloghi n. sp.

(PLATE I, *Figs. 1—3*)

1

2

3

Material: Specimens UGP. 226a, b
Holotype: Specimen UGP. 226a, pictured in Plate I, *Figs. 1—3*
Locus typicus: Railway-cut Nr. 5. northeast Nagyvisnyó
Stratum typicum: Upper Permian, Codonofusiella-zone
Derivatio nominis: Named after K. BALOGH
Diagnosis: Species of Peronidella with an elongated shape and a large cloaca.

Description: The sponges occur singly or loosely compounded. Their shape is elongate-cylindrical with a large, round, osculum at the summit. The type-specimen is more than 90 mm in hight and 55×40 mm in cross-section; inarticulate cylindrical cloaca of these specimens are more than 80 mm in hight with an osculum having a cross-section of 18×12 mm. Fused triacts from 0,05 mm to 0,2 mm in thickness from the open tissue of the wall. The primary triact structure cannot be seen due to a strong recrystalliz at ion of the fibers, but the primary triact nature is shown the occurence of knots always having three rays at the skeleton. Aporrhyses and epirrhyses are not present.

Remarks: The inarticulate body of the sponge is typical for the *Inozoa* ZITTEL. The cylindrical shape of the cloaca, the lack of canals within the wall and the construction of the tissue composed of triacts are feature of the genus Peronidella. — Until now this genus has not been described from the Permian.

AGE OF THE BEDS WITH PERONIDELLA

The beds with Peronidella belonging undoubtedly to the higher part of the Upper Permian, are overlain after a few meters by Neogene sediments. Therefore a gap of unknown extension separates the Permian of this outcrop from the Lowermost Triassic of its surroundings, here. After BALOGH, however, this gap between the two formations can correspond to an uppermost Permian sequence of 30—35 m in thickness that appears in other localities characterized with Waagenophyllum.

In my opinion, the brachiopod-fauna of the "Lyttonia-beds" of the Bükk is to correlate to the Upper Permian faunas of Transcaucasia and Iran with *Leptodus nobilis* WAAGEN, *L. richthofeni* (KAYSER), *Spinomarginifera helica* (ABICH), *Tschernyschewia typica* STOYANOV and *Tyloplecta yangtzeensis* (CHAO). These forms occur in the Djulfa-region in the Araxilevis/Araxoceras zone of the Djulfian [RUZHENTSEV, 1965], in Central Albroz in the Tyloplecta zone of the Upper Nesen formation [STEPANOV *et al.*, 1969], in Central-Iran in the unit 4 of the Abadeh formation [Taraz, 1971]. This association is named by WATERHOUSE [1971] the Baisalian fauna. Following ROSTOVTSEV & AZARYAN [1971] and WATERHOUSE [1971], the Permian/Triassic boundary should be drawn between the Paratirolites zone and the Claraia beds. The Dorshamian stage of Djulfa to be found between the Araxoceras zone

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PLATE I
Peronidella baloghi n. sp. Holotype

Fig. 1. Vertical section 1,3×
Fig. 2. Vertical section 1,3×
Fig. 3. Exterior transverse view 1,3×

and this boundary has a max. thickness of 70 m. It is therefore possible that in the Bükk-Mountains, the gap above the "Lyttonia-beds" corresponds to the Dorsham stage of Transcaucasian.

As mentioned above, BALOGH [1964] raised the possibility that the beds with Waagenophyllum, occuring south of Nagyvisnyó (in the Nyárjuhegy) at great length along the boundary-line between the superficial extents of Permian and Triassic, are younger than the "Lyttonia-beds", and represent the Uppermost Permian. Unfortunatelly, the specimens of this coral from Nyárjuhegy have been flattened out by strong tectonic movements. The corallities are small (max. 5—6 cm in diameter) and have 14—19×2 septa. The same corals were described by F. HERITSCH [1944] from the quarry next to the railway-station Nagyvisnyó as *Waagenophyllum indicum mongoliense*, but a revision of this material by H. FLÜGEL [1970] has shown, that they belong probably to *Waagenophyllum kueichowense* or *W. huangi*. Namely, *Waagenophyllum indicum* has a greater (6—8 mm) diameter and more septa (20 and more ×2), than the mentioned forms.

Obviously the *Waagenophyllum*-occurrences at the railway-station belong to a deeper horizon than that of the Nyárjuhegy. Some difficulties, however, are caused by the fact that the genus *Waagenophyllum* appears in the lower beds of the railway-cut Nr. 5, in a pretty depth below the "Lyttonia-beds", as well. Therefore it is to raise if the *Waagenophyllum*-limestone of Nyárjuhegy and that of the lower part of the railway-cut Nr. 5 should have the same age.

Together with *Peronidella baloghi* also *Codonofusiella* sp. occurs in the railway-cut Nr. 5. This foraminifer is typical for the beds below the Araxilevis zone in Djulfa. RUZHENTSEV [1965] was of the opinion that the Codonofusiella zone belongs to the base of the Djulfian, whereas STEPANOV *et. al.* [1969] interpreted the Codonofusiella zone as the top of the Khachikian. Following WATERHOUSE [1971] this zone is characterized by the Kathwai-fauna that includes the uppermost representatives of *Waagenophyllum* in this section, too.

Relying upon these findings the present author correlates the stratigraphical position of the Latest Permian beds of the railway-cut Nr. 5 near Nagyvisnyó compared to to that of the Djulfa region as presented on the Table 1.

TABLE 1

Stage	Faunal horizont of Waterhouse	Iran/Transcaucasia	Railway-cut Nr.5 near Nagyvisnyó (Bükk-Mountains)
Djulfian	Makarewan Ogbian Vedian	Dorsham stage	?
	Baisalian	*Vedioceras Araxoceras Araxilevis* *Tyloplecta*-fauna	*Lyttonia* beds
Guadalupian	Kathwai	*Codonofusiella* zone	Underlay of the „*Lyttonia* beds"

ACKNOWLEDGEMENTS

During my stay in the Bükk-Mountains in autumn of 1972 I had the opportunity to become acquainted with the Palaeozoic beds of this district under the guiding of PROF. DR. K. BALOGH. I express my thanks to him for his valuable help. Thanks are also due to PROF. DR. J. FÜLÖP, President of the Geological Survey of Hungary, for the organization of the trip.

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CONTRIBUTIONS TO THE ALKALINE PERMANGANATE OXIDATION OF THE KEROGEN, LIGNITE AND PEAT

GY. GRASSELLY, M. HETÉNYI and M. AGÓCS

INTRODUCTION

Investigations concerning the oxidation of the kerogen and other organic materials of the sediments play an important role in studying the structure and behaviour of the kerogen and the different organic remnants of sedimentary rocks.

These investigations are directed partly to the identification of soluble products of alkaline permanganate oxidation of organic materials isolated from sediments partly to the determination of the ratio of the different components formed to enable to conclude the structure of the kerogen, at least that of its oxidized part. The non-oxidized part remained, however, have not been investigated in a similarly detailed manner.

PRODUCTS OF THE ALKALINE PERMANGANATE OXIDATION

The oxidation by alkaline permanganate was applied investigating the structure of coals by BONE *et. al.* [1934]. The coals could be oxidized easily and totally, only in the case of anthracite remained a little rest unoxidized. In the series peat — anthracite the presence of benzene carboxylic acids in an increasing amounts besides CO_2, oxalic acid, acetic acid could be stated by the authors.

DOWN and HIMUS [1941] employing the method to the investigation of kerogen stated on the basis of the oxidation products that some of the kerogens are very similar to the coals and in these samples aromatic structure was to be suggested, whereas in kerogens of other origin e. g. in that of the Colorado oil shale and the Estonian oil shale kerogen (kukersite) the aromatic structure was not present or played merely a subordinated role. Among the oxidation products of the first group the non-volatile non-oxalic acids were present only below 1% and they were present similarly in a very small amounts in the oxidation products of the Estonian kerogen, too [ROBINSON *et al.*, 1953; FOMINA and POBUL, 1955]. It has been demonstrated that materials with highly condensed aromatic structure as for example the anthracite produce non-volatile non-oxalic acids (benzene carboxylic acids) in significant amounts, whereas the fatty materials are resistant to the oxidation. This fact alone renders possible some differentiation among the kerogens of different origin.

According to ROBINSON [1969] the Green River kerogen could be oxidized nearly totally to CO_2, oxalic acid and volatile acids demonstrating that it does not contain fatty material or condensed aromatic structures in a remarkable amount. On the contrary, the Middle Dunnet kerogen (Scotland) produced 14% non-volatile

non-oxalic acids pointing to the presence of aromatic structures or at least to the presence of structures able to form aromatic acids during the oxidation. The torbanite from Australia was very resistant to the oxidation owing to its considerable fatty material content.

However, during the oxidation the intermediate products themselves can be oxidized, therefore, to identify the intermediate products the step-oxidation was employed. Many authors dealt with the investigation of the products of the step-oxidation and a series of intermediate products were identified. According to the summary of STEFANOVIČ and VITOROVIČ [1959] among the oxidation products the "regenerated humic acids" [ROBINSON, HEADY, HUBBARD, 1953]; besides the non identified complex acids of higher molecular weight a mixture of dicarboxylic acids ranging from the oxalic acid to the adipic acid [ROBINSON, CUMMINS, STANFIELD, 1956]; volatile monocarboxylic acids, dicarboxylic acids from oxalic to azelaic acids and viscous acids of unknown composition [FOMINA, POBUL, 1955] can be found.

According to STEFANOVIČ and VITOROVIČ the oxidation with potassium permanganate in acetone solution is more suitable being this a more specific oxidizing agent and the oxidation of the kerogen by potassium permanganate occurs at definite points susceptible to oxidative attack [DJURICIČ, MURPHY, VITOROVIČ, BIEMANN, 1971].

INVESTIGATION OF NON- OXIDIZED PART

The bulk of investigations of the products obtained by total or step-oxidation was directed mainly to the identification of the products, however, very few data can be found in the literature concerning the non-oxidized part remained after the single steps of oxidation. It may be assumed that besides the study of the oxidation products the investigation of this non-oxidized part may also contribute to the knowledge regarding the structure of kerogen.

The change of the elemental composition of the Estonian oil shale kerogen during its oxidation was reported by FOMINA, POBUL and DEGTEREVA [1965]. According to them the network of kerogen remained unchanged during the oxidation. This opinion is supported by the fact that the C and H content as well as the amount of the heteroatoms remained essentially unchanged in the oxidation rest after 8—72 hours oxidation even if more than 90 percent of the kerogen transformed into soluble oxidation products. Splitting off saturated structure units would have been revealed by decrease of the hydrogen content. As this decrease could not ben stated, according to FOMINA *et al.*, the more kerogen is degraded into soluble oxidation products the more structure units with saturated chains remain.

According to DOWN and HIMUS some of the kerogens contain two types of material, one of them is easily oxidizable by alkaline permanganate, the other one is resistant to this action. According to DJURICIČ *et al.*, [1971] the structure of the Green River kerogen consists of a "nucleus" of interconnected long aliphatic methylene bridges to which unbranched and isoprenoid chains are attached and these branching points are susceptible to permanganate oxidation. In this conception the production of mono- or dicarboxylic acids depends upon whether the splitting off occurs at a branching point of a saturated side-chain or at two carbon atoms connected by a methylene bridge.

At any rate, it would be interesting to attempt the characterization of changes taken place in the rest remained undissolved during the step-oxidation. If the structure

of kerogen remains either unchanged or some changes occur as for example the relative increase of ratio of saturated structures or on contrary the splitting off saturated side-chains, lost of some functional groups or fission or recombination of bonds, these changes will presumably be reflected either by IR spectra or by derivatographic examinations.

To approach the solution of this problem Estonian oil shale kerogen, peat and lignite were stepwise oxidized by alkaline permanganate during relatively short time and the rest remained undissolved after the single steps was investigated chemically as well as by derivatographic method and IR-spectroscopy to attempt to characterize the changes taken place during the oxidation.

EXPERIMENTAL PART

Determination of C and H content

The soluble organic material of the samples was extracted by chloroform in a Soxhlet-apparatus, then portions of 0,5—0,5 g was weighed into Erlenmeyer flasks and the oxidation was carried out at 50 °C by alkaline permanganate solution (1% KOH and solid potassium permanganate from 0,1 g increased to 2 g in the successive steps).

The rest of permanganate was eliminated by treatment with sodium sulfite in a weakly acidified solution. After filtration and washing with hot distilled water the rest was dried at 60 °C. The oxidizable organic carbon of these samples was determined by wet method. 0,01 g was weighed in a mixture of 10 ml N $K_2Cr_2O_7$ and 15 ml $Ag_2SO_4 - H_2SO_4$ solution (25 g Ag_2SO_4 in 1 l concentrated H_2SO_4). The solution was heated for one minute to 150 °C. After cooling the solution was filled up to 200 ml with distilled water and 10 ml 85% phosphoric acid and 0,2 g NaF was given to it and the excess of $K_2Cr_2O_7$ was titrated by Mohr-salt solution against diphenylamine indicator. Each series requires a blank titration.

$$C_{org} = \frac{\left(\begin{array}{c}\text{ml Mohr-solution—ml Mohr-solution} \\ \text{for the blank} \qquad \text{for the sample}\end{array}\right) \cdot 0{,}3}{\text{g sample weighed in}}$$

For the determination of the C_{org} and H one part of the samples was treated by diluted HCl and some drops of diluted hydrogene peroxide. After filtering and washing the samples were dried at 60 °C. These samples served for the C—H analysis by combustion in oxygen as well as for IR investigation and DTA investigations.

The organic C content oxidizable by wet method as well as the total organic C and H content determined by the combustion method in the original samples and the undissolved rests after the single steps of oxidation are shown in Table 1.

Comparing the carbon content obtained by wet method and by combustion in oxygen, respectively, it is conspicuous that the difference between the two values increases by the duration of step-oxidation. The carbon content of the starting Estonian oil shale kerogen determined either by wet oxidation or by combustion method is nearly the same (75,1% and 75,8%), however, after 24 hours oxidation the carbon content oxidizable by wet method amounts to only 6,4%, though the total C_{org} by combustion is 65,8%. A similar situation can be observed also at the peat and lignite, though in the carbon content determined in the starting samples

TABLE 1

C and H content of the starting samples and the undissolved rests after the single steps of oxidation by alkaline permanganate solution

Duration of alkaline permanganate oxidation	Estonian oil shale kerogen				Lignite				Peat			
	C_{org} % by wet oxidation	C_{org} % by combustion	H % by combustion	H/C atomic ratio	C_{org} % by wet oxidation	C_{org} % by combustion	H % by combustion	H/C atomic ratio	C_{org} % by wet oxidation	C_{org} % by combustion	H % by combustion	H/C atomic ratio
Starting samples	75,1	75,8	9,2	1,46	45,5	55,5	5,2	1,13	45,2	52,2	6,0	1,37
10'	74,4	—	—	—	44,1	—	—	—	44,5	—	—	—
30'	57,1	—	—	—	33,3	53,3	5,2	1,16	29,5	47,3	6,0	1,51
60'	43,2	68,2	8,1	1,42	22,2	54,1	5,3	1,18	25,0	46,6	5,9	1,53
90'	—	—	—	—	11,1	—	—	—	—	18,6	—	—
120'	23,1	67,3	8,2	1,47	1,6	21,0	5,0	2,85	3,2	32,3	4,6	1,71
24h	6,4	65,8	7,8	1,43	—	—	—	—	—	—	—	—

by wet method and by combustion already a little difference can be stated being the carbon content by wet method some per cent lower than that by combustion. This difference increases by advancing oxidation, *e.g.* in the case of peat after 2 hours oxidation the carbon content of the rest determined by wet method amounts to 3,2%, whereas the total C_{org} by combustion is 32,3%.

Investigating the H content of the oxidation rests and the starting materials it can be stated in accordance with the observation of FOMINA *et al.* that the decrease of the hydrogen content during the oxidation is very small, in the case of kerogen after the first treatment appears 1% decrease, the H content after the further steps shows nearly no change; the difference in the H content of the single lignite samples is negligible, in the case of peat the decrease in H content after the oxidation steps is somewhat more considerable (in the starting material 6,0% and after 120 minutes oxidation 4,6%).

As to the possible interpretation of these experimental data, the statements of different authors agree that the Estonian oil shale kerogen has a rather aliphatic character and contains very little or no benzenoid structures. The aromatic structures as well as the saturated units are more resistant to the wet oxidation than the unsaturated bonds. In FOMINA's opinion at progressing decomposition of the kerogen during the step oxidation the amount of saturated chain units will increase in the rest. This opinion is supported by the fact mentioned above, by the difference between the total C_{org} by combustion and the C_{org} oxidizable determined by wet method which difference increases by the progressing oxidation.

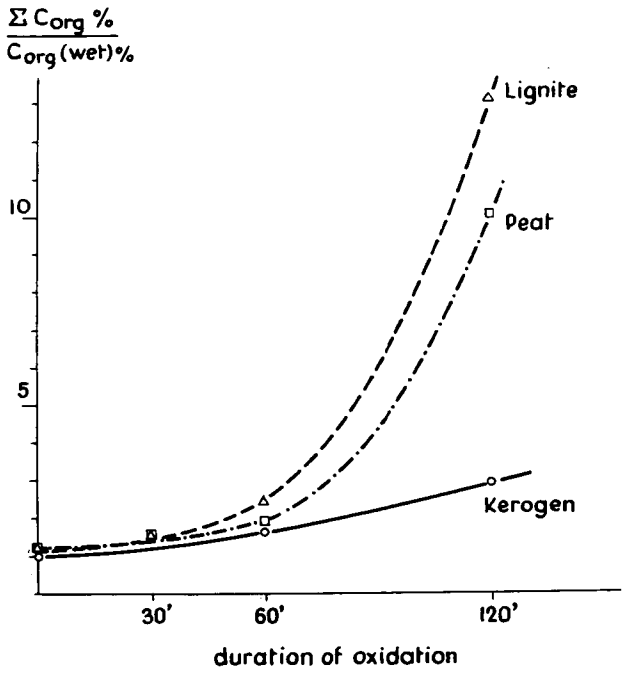

Fig. 1. The change of the quotient of total carbon content determined by combustion and the carbon content oxidizable by wet method in function of the duration of oxidation

The carbon content determined by wet oxidation may represent the carbon in more easily oxidizable bonding that is first of all the unsaturated bonds, whereas the total carbon content determined by combustion in oxygen involves the carbon content of unsaturated, saturated and aromatic structures.

Considering the *Fig. 1* and the data of Table 1 it may be stated that in the case of kerogen within the oxidation period applied the quotient of the carbon content of two kinds increases approximately uniformly. It may be interpreted according to FOMINA *et al.* that during the progressive oxidation of the kerogen the amount of the saturated chain units not oxidizable by wet oxidation uniformly increases in the undissolved rest. On the other hand, the change of the quotient is much more significant in the case of peat and lignite and the carbon content oxidizable by wet method amounts to merely 3,2% in the oxidation rest of peat and 1,6% in that of lignite after 120 minutes oxidation, whereas the same value for the kerogen is 23,1%. The total carbon content determined by combustion in the undissolved rest of the samples oxidized for 2 hours, expressed in percentage of the total carbon content of the starting samples: kerogen 88,8%, peat 61,9% and lignite 37,8%, *i.e.* within the given time interval the degradation and transformation of the kerogen into soluble oxidation products is relatively slow, whereas that of the lignite far faster process.

As shown in Table 1 the hydrogen content of the peat samples treated decreases by the duration of oxidation and the amount of carbon content oxidizable by wet method diminishes more and more by progressing oxidation compared to the amount of total C_{org}. A similar tendency can be found also at the lignite samples, however, the hydrogen content of the samples treated remains practically unchanged. The decrease of the total carbon content is much slower than the decrease of the carbon content oxidizable by wet method which may be interpreted by the benzenoid structures originally present and by the relative increase of the amount of aromatic structures partly by the relative increase of the rate of saturation.

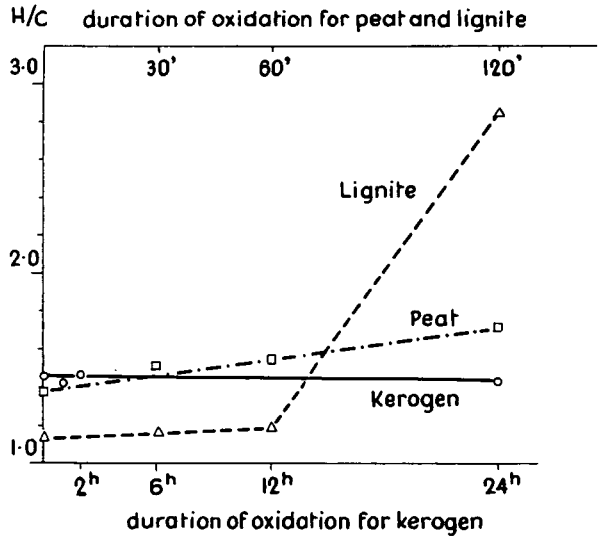

Fig. 2. H/C ratio during the oxidation of kerogen. peat and lignite

As it is shown by *Fig. 2* the H/C atomic ratio is practically unchanged during the 24 – hours step-oxidation in the case of kerogen and ony a slight increase of the H/C ratio can be stated at the peat samples. Similarly a slight increase of the H/C ratio is exhibited by the lignite samples in the first hour of oxidation, then increases rapidly since the H content remains practically unchanged and at the same time the carbon content decreases significantly.

Infrared spectra of the samples

The IR investigations were carried out by UNICAM SP 200 spectrophotometer. The wavenumbers and estimated intensities of absorption bands observed on the spectra of the starting samples are shown in Table 2—4 and the spectra in *Figs. 3—5.*

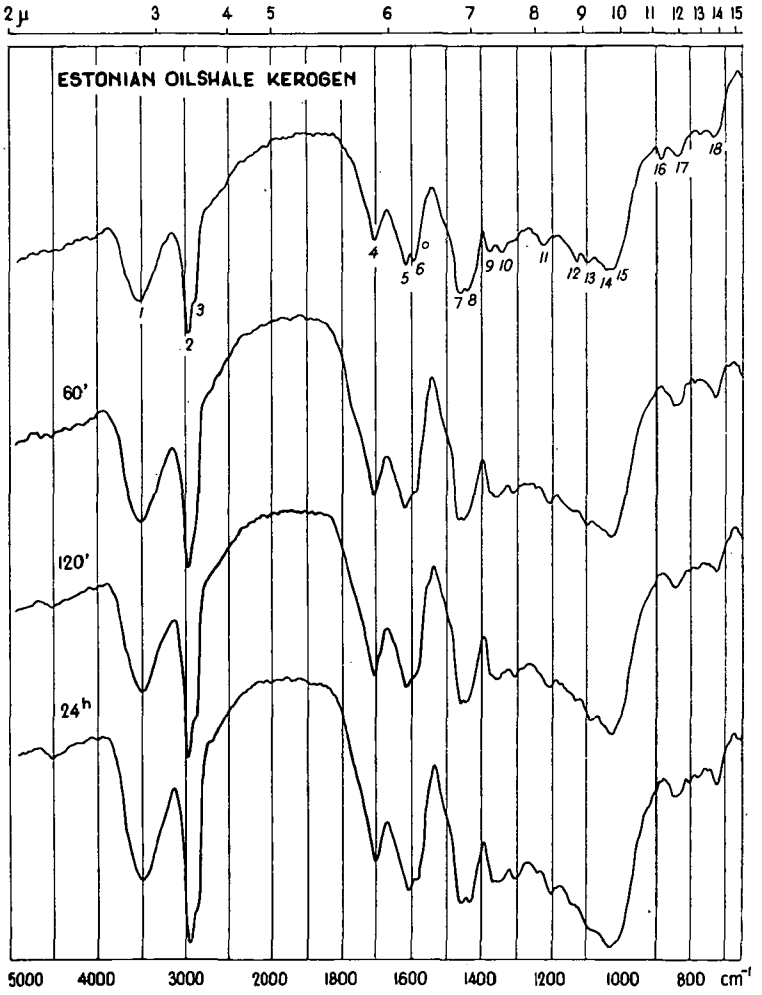

Fig. 3. IR spectra of kerogen samples (the first curve is that of the starting sample, the others those of samples oxidized for periods denoted on the curves)

TABLE 2

Wavenumbers and estimated intensities of absorption bands of IR spectrum of the kerogen

N°	Band positions (cm^{-1})		
1.	3500 s (broad)	νOH	
2.	2980 vs	$\nu(=CH)$	aromatic
		$\nu_{as}CH_2$, $\nu_{as}CH_3$	aliphatic
		$\nu(=CH_2)$, $\nu(=CH)$	olefin
3.	2880 s	ν_sCH_2, ν_sCH_3	aliphatic
4.	1710 m	$\nu C=O$	carboxylic group
5.	1620 s	$\nu C=C$	olefin
		$\nu_{as}CO_2$	carboxylate anion
		νCC	aromatic
6.	1590 s	$\nu C=C$	olefin
		νCC	aromatic
		ν_sCO_2	carboxylate anion
7.	1470 s	νCC	aromatic
		$\delta_{as}CH_3$	aliphatic
8.	1440 s	νCC	aromatic
		$\delta_{as}CH_3$	aliphatic
		β_sCH_2	aliphatic
9.	1380 w	δ_sCH_3	aliphatic
		νCO_2	carboxylate anion
10.	1340 w	δ_sCH_3	aliphatic
11.	1220 w	$\nu C_{Ar}—C(=O)$	aromatic carboxylic acid
12.	1130 vw	$\nu C—O(H)$	tertiary and phenolic OH
13.	1100 vw	$\nu C—O—C$	esters with conjugated double bonds
14.	1040 w		
15.	1020 w		
16.	880 w	$\gamma(=CH)$	olefin
17.	830 w	$\gamma(=CH_2)$	
18.	730 w	$\gamma(=CH)$	aromatic

TABLE 3

Wavenumbers and estimated intensities of absorption bands of IR spectrum of the lignite

N°	Band position (cm^{-1})		
1.	3450 vs (broad)	νOH	
2.	3000 s	$\nu(=CH)$	aromatic
		$\nu_{as}CH_2$, $\nu_{as}CH_3$	aliphatic
		$\nu(=CH_2)$, $\nu(=CH)$	olefin
3.	1710 vw	$\nu C=O$	carboxylic group
4.	1610 s (broad)	$\nu C=C$	olefin
		$\nu_{as}CO_2$	carboxylate anion
		νCC	aromatic
		βOH	
5.	1520 s	νCC	aromatic
6.	1470 w	νCC	aromatic
		$\delta_{as}CH_3$	
7.	1440 vw	$\beta_s CH_2$	aliphatic
		$\delta_{as}CH_3$	aliphatic
		νCC	aromatic
		βOH	combination band of carboxylic acid
		$\nu C—O$	
8.	1370 vw	$\delta_s CH_3$	aliphatic
		$\nu_s CO_2$	carboxylate anion
9.	1270 m	$\nu C—O$	carboxylic acids
		βOH	
10.	1210 vw	$\nu C_{Ar}—C(=O)$	aromatic carboxylic acid
11.	1140 m	$\nu C—O(H)$	tertiary and phenolic OH
12.	1100 w	$\nu C—O—C$	esters conjugated with double bonds
13.	1030 w		
14.	830 m	$\gamma(=CH)$, $\gamma(=CH_2)$	olefin
15.	750 m	$\gamma(=CH)$	aromatic

Considering the IR spectra of the samples investigated and comparing the tpectra of samples oxidized for different periods to that of the starting sample, she changes can be summarized as follow:

The IR spectrum of the kerogen exhibits a great number of absorption bands. The spectra of the samples oxidized points to that during the oxidation no significant changes occurred. At least merely the bands 5 and 6 exhibit a slight change in intensity comparing to that of the starting sample. In the spectrum of the starting kerogen sample three weak bands can be established within the interval 1000—1100 cm^{-1} which more and more overlap during the treatment and at last they appear as an intensive, broad band. This may be attributed to the C—O—C vibration of esters conjugated with double bond. In the spectrum of the starting sample the bands characteristic of —OH and —COOH groups are also observed and their intensity

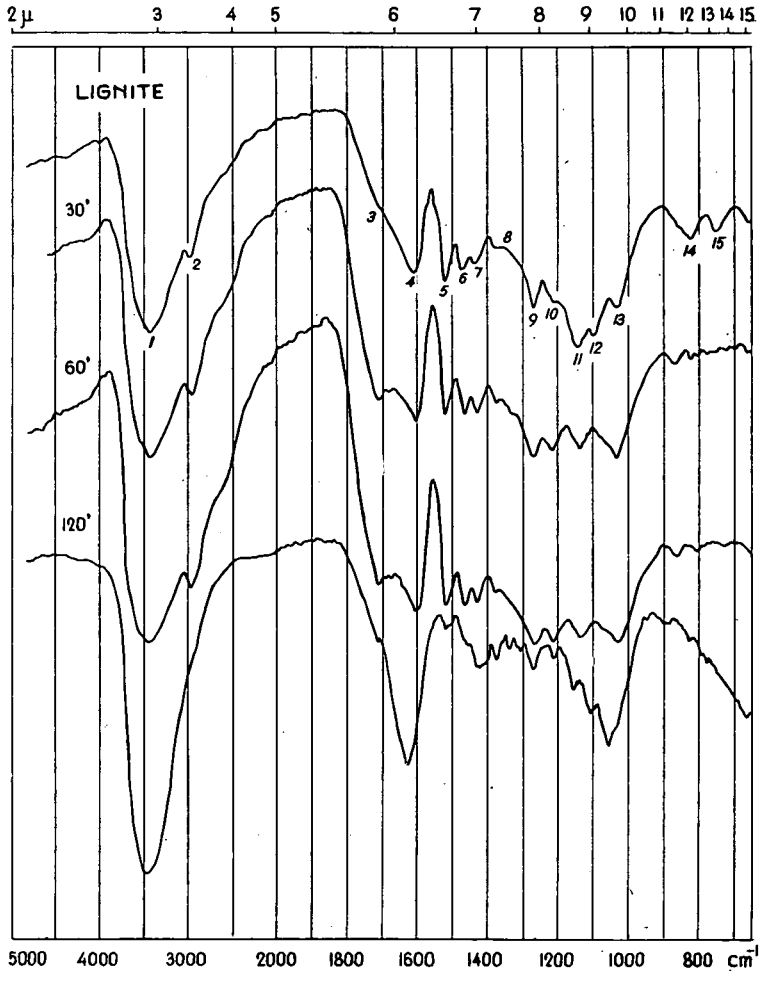

Fig. 4. IR spectra of the lignite samples (the first curve ist that of the starting sample, the others those of samples oxidized for periods indicated on the curves)

TABLE 4

Wavenumbers and estimated intensities of absorption bands of IR spectrum of peat

N°	Band positions (cm^{-1})		
1.	3450 vs (broad)	νOH	
2.	2980 m	$\nu(=CH)$	aromatic
		$\nu_{as}CH_2$, $\nu_{as}CH_3$	aliphatic
		$\nu(=CH)$, $\nu(=CH_2)$	olefin
3.	1720 vw	$\nu C=O$	carboxylic group
4.	1640 s (broad)	$\nu C=C$ βOH	olefin
5.	1540 vw	$\nu_{as}CO_2$	carboxylate anion
6.	1250 m	$\nu C—O$ βOH	combination band of carboxylic acids
7.	1150 w	$\nu C—O(H)$	tertiary and phenolic OH
8.	1050 s (broad)	$\nu C—O—C$	esters conjugated with double bond

shows no essential change during the treatment. The essentially unchanged character of the spectra of the kerogen samples seems to support the statement of FOMINA *et al.* [1965], the network of the kerogen remains unchanged during the step-oxidation, the H content as well as the H/C ratio exhibit also merely a negligible change during the oxidation, reported in this paper, too.

Comparing the spectra of the starting and oxidized lignite samples a more definite difference can be established. The intensity ratio of bands at 3450 cm^{-1} and 2980 cm^{-1} is nearly the same in the first step, however, after 2 hours treatment the band at 2980 cm^{-1} disappears almost totally and the intensity of the band at 1710 cm^{-1} exhibits a very slight increase. This band may be attributed to the C=O vibration. A more definite increase in intensity is exhibited by the band at 1610 cm^{-1} which may be originated either from olefin bond or aromatic structure or from moisture or carboxylate anion. The change between 1000—1100 cm^{-1} mentioned already at the kerogen spectra can also be observed on the spectra of the lignite samples.

The greatest differences between the spectra of the starting and treated samples are exhibited by the peat samples. The strong increase of the intensity of the band at 2980 cm^{-1} points to the relative increase of the amount of CH_2 and CH_3 groups.

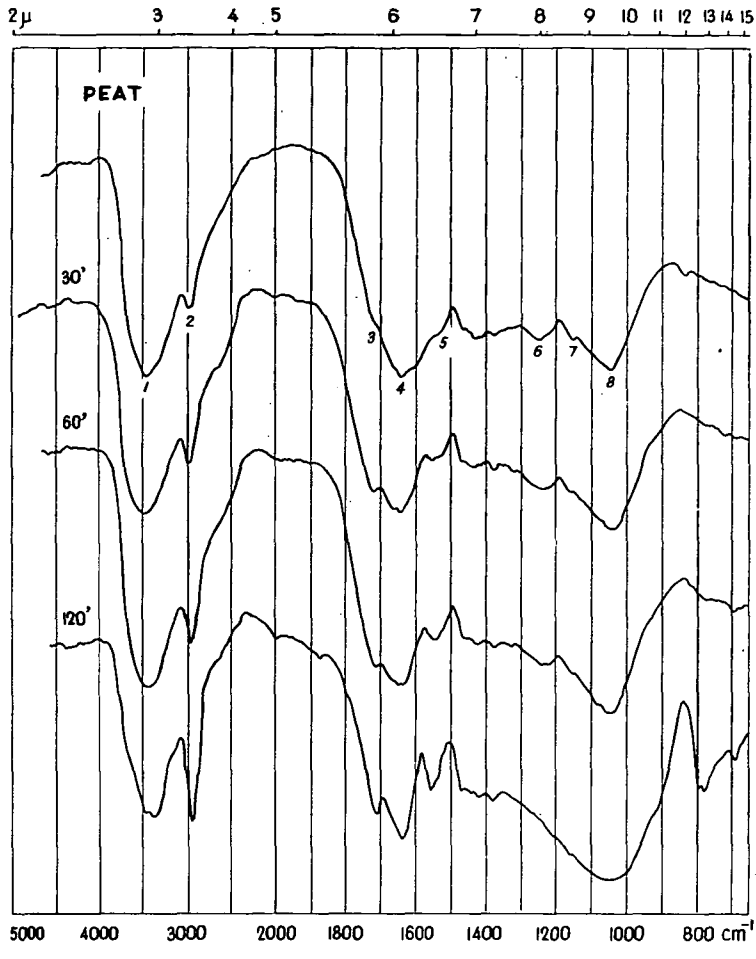

Fig. 5. IR spectra of peat samples (the first curve is that of the starting peat sample, the others those of samples oxidized for periods indicated on the curves)

The intensity ratio of the bands at 3450 cm^{-1} and 2980 cm^{-1} in the starting sample is 4,00 whereas in the spectra of the sample oxidized for two hours is merely 1,05. An increase of the intensities of bands at 1540 cm^{-1} and 1720 cm^{-1} can also be established. The first may be due to the carboxylate anion vibration and the latter due to C=O bond pointing to possibly the relative increase of the amount of aromatic carboxylic acids. Amongs the three materials the formation of esters seems to be the most expressed in the case of the peat.

DTA investigations of the samples

The differential thermal analysis of the samples was carried out by ERDEY—PAULIK "Derivatograph". The DTA and DTG curves of the starting and oxidized samples are shown in *Figs. 6—8.*

It is true that the trend and rate of the thermal decomposition of organic compounds is controlled by the energies of bonds existing in the compound and also it is known that *e. g.* the compounds with alcoholic OH groups or the carboxylic group have a lower thermal stability than e. g. the methyl-, methoxy- etc. groups or at higher temperatures the aromatic structures have a greater thermal stability

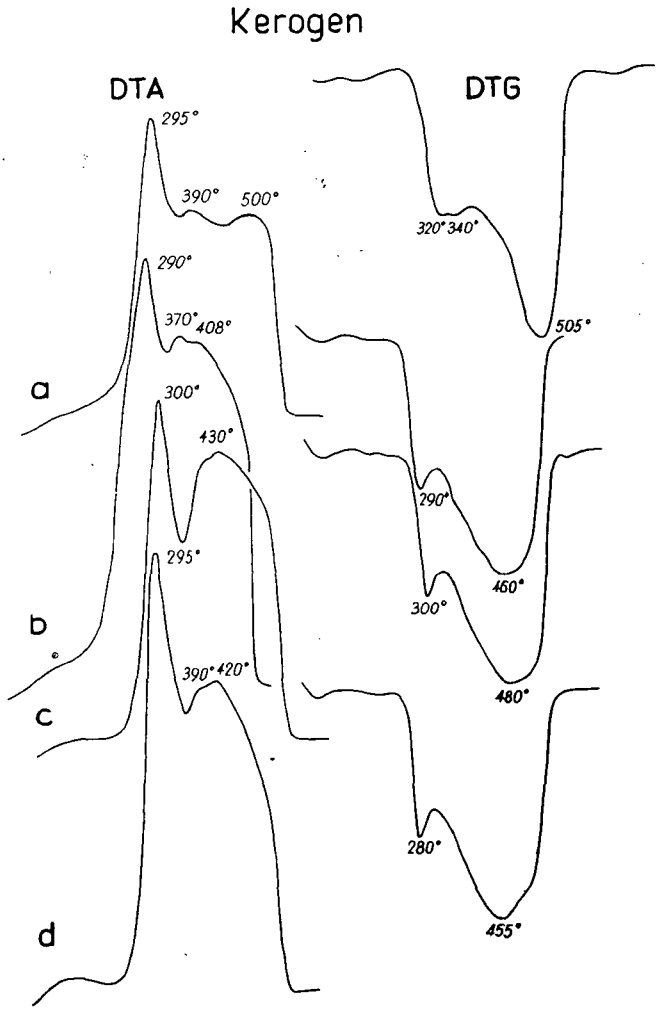

Fig. 6. DTA and DTG curves of the kerogen samples: a) starting sample, b—d) undissolved rest of samples oxidized for 1,2 and 24 hours

than the aliphatic ones. In spite of all the interpretation of the DTA curves of such complicated organic materials as represented by the investigated ones is a fairly difficult task.

It has to taken into consideration that during the thermal decomposition a series of reaction products may be formed and the solid material and the volatile

components can react with each other, the degradation products themselves may suffer a further gradual degradation and compounds of greater thermal stability may also be formed by the possible recombination of bonds.

Therefore, it was merely aimed to use the DTA and DTG curves for a qualitative comparison of the starting samples and those of oxidized for different periods to establish the changes taken place in the samples during the step-oxidation.

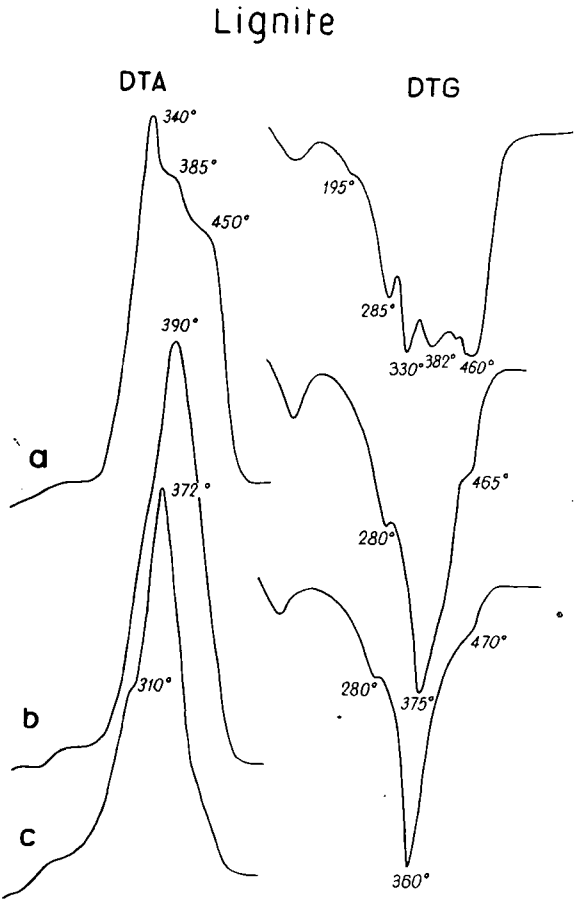

Fig. 7. DTA and DTG curves of the lignite samples: a) starting sample, b—c) undissolved rest of samples oxidized for 30 and 60 minutes, respectively

The DTA and DTG curves of the kerogen samples seems to be in accordance with the statements on the basis of IR spectra inasmuch merely a very little change during the oxidation can be observed. The DTA and DTG curves of the samples oxidized for 1, 2 and 24 hours exhibit nearly the same character, the temperature of the main exothermic DTA peak shows only a very little fluctuation between 290—300 °C and the same is valid for the first DTG peak, it varies between 280—300 °C. It is to mention that the temperature of the first exothermic DTA peak of

the untreated sample is also between 290—300 °C. It may be originated from components remained unchanged during the oxidation by alkaline permanganate, e. g. perhaps by the oxidation of OH and COOH groups as well as the splitting off the methyl- and methylen groups. The vibration of these groups on the IR spectra show namely no remarkable changes in their intensities during the oxidation.

As to the DTA and DTG curves of the lignite samples, considerable differences can be stated among those of the starting samples and those oxidized for 30 and 60 minutes, respectively. The DTA and DTG curves of the starting samples comparing to those of the samples oxidized merely for 30 minutes exhibit already a very definite difference. The DTA and DTG curves of the starting sample show overlappings of more peaks, whereas the curves of the oxidized samples exhibit more simple peaks characteristic of lignin demonstrating that most part of the other components present in the original sample turned into soluble products already at the beginning of the oxidation with alkaline permanganate. The curves of the samples treated are very similar to each other as the IR spectra of samples oxidized for 30 and 60 minutes, respectively, are also very similar.

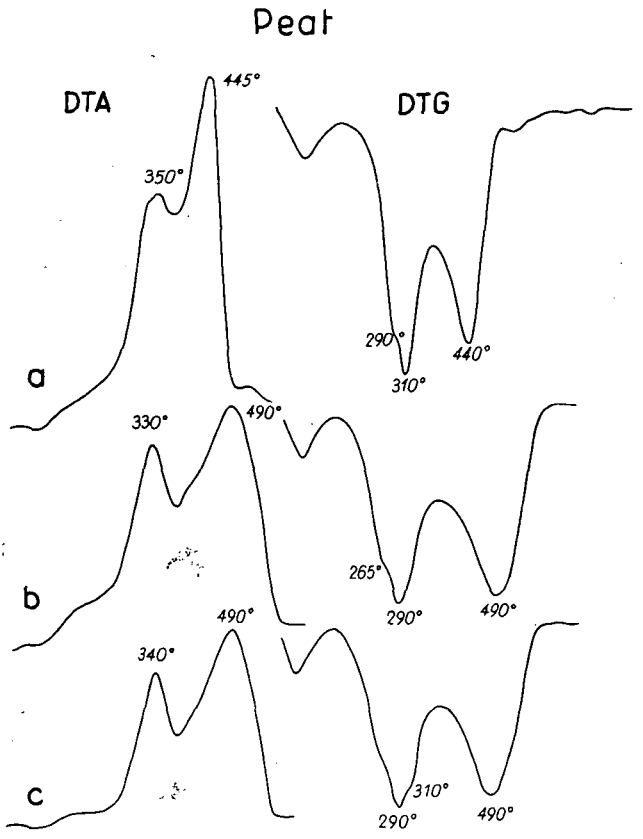

Fig. 8. DTA and DTG curves of the peat samples: a) starting sample, b—c) undissolved rest of the samples oxidized for 30 and 60 minutes, respectively

The DTA and DTG curves of the peat samples are fairly simple. According to F. PAULIK and J. PAULIK [1958] in the first step the thermal decomposition of cellulose and hemicellulose components may be assumed followed by the decomposition of the other components as lignin and/or humic material.

The curves of the samples oxidized for 30 and 60 minutes, respectively, echibit almost the same character, however, they differ from the curves of the original sample, especially in the temperature of the second peak. It is to mention that the IR spectra of the peat samples oxidized for the time mentioned are also nearly identical but they also show some definite difference compared to that of the starting material.

SUMMARY

Considering the results of this preliminary investigations reported the followings can be established:

1. The statement of FOMINA *et al.* that the structure of the Estonian oil shale kerogen remains essentially unchanged during the step-oxidation by alkaline permanganate and that the constancy of the hydrogen content may be interpreted by the relative increase of saturated units seems to be supported also by the present investigations. The IR spectra and DTA—DTG curves of the starting kerogen sample and those oxidized for 1—2—24 hours exhibited only very small changes and the hydrogen content as well as the atomic H/C ratio showed also negligible variations.

2. The increasing difference between the total C_{org} determined by combustion in oxygen and the carbon content oxidizable by wet method determined in the same samples after the single steps of oxidation may be a qualitative measure of the relative increase of structural units more resistant to oxidation. Plotted the quotient of the $\Sigma C_{org}\%$ and $C_{org(wet)}\%$ against the oxidation period, characteristic curves for the three materials are obtained. This simple way perhaps may be useful in the characterization of insoluble organic materials of sedimentary rocks.

3. The IR spectra and the DTA—DTG curves of the starting samples and those of oxidized for different periods demonstrate that the kerogen samples suffered only a very little change during the oxidation, whereas also a little but better pronounced change can be observed at the lignite and the peat, especially comparing the curves of the samples oxidized to those of the starting samples. At any rate, during the step-oxidation with alkaline permanganate the solid rest remained undissolved suffers a slight change already at the beginning of the oxidation, however, the progress of this alteration is a fairly slow process. The IR spectra of the samples treated for 30 and 60 minutes, respectively, are similar and only a very slight change in intensities of some absorption bands may be established by the progressing oxidation.

4. Investigations of the behaviour of undissolved rests of samples after prolonged step-oxidation by alkaline permanganate are in progress. It seems to be also advisable to carry out the IR investigation of the starting and oxidized samples heat treated at temperatures corresponding to the temperatures stated on the DTA and DTG curves to enable to trace the possible steps of the thermal decomposition of the samples (cleavage of some bonds, recombination of bonds, lost of some functional groups etc.) owing to extend the applicability of the DTA and DTG investigation of such material also for semi-quantitative interpretation.

ACKNOWLEDGEMENT

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ON THE GENESIS OF LOWER OLIGOCENE MANGANESE DEPOSITS IN GEORGIA

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On the territory of Western Georgia numerous deposits and shows of manganese, silicite and phosphorite are known at the base of the Lower Oligocene *(Fig. 1)*. These minerals occur in a close association and there is no doubt about their genetic relations.

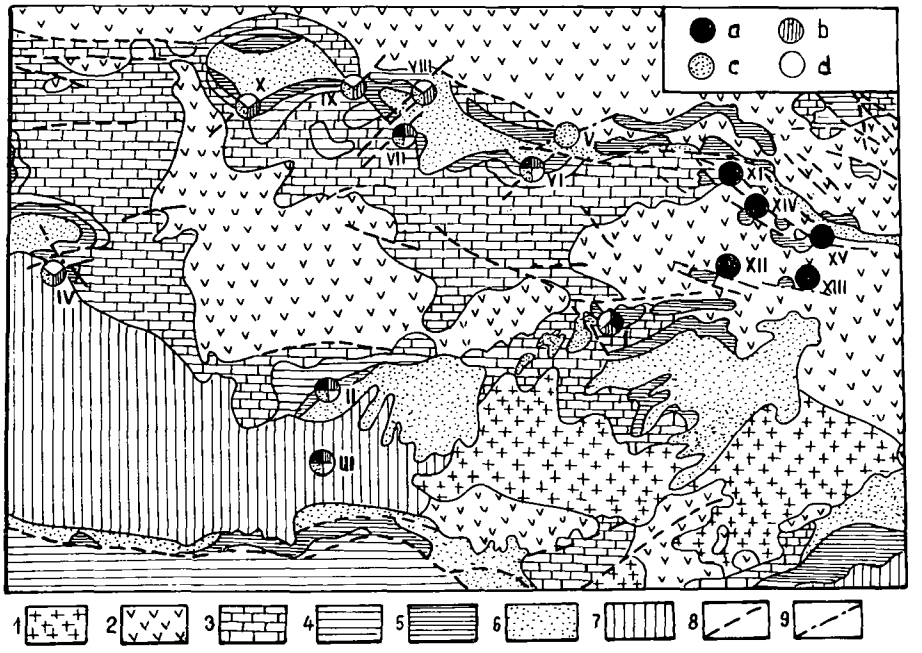

Fig. 1. Distribution scheme of Lower Oligocene deposits and ore shows of Mn, Si, Fe and P in Western Georgia.

1 — crystalline rocks of Dzirulsk massif; *2* — the Jurassic; *3* — the Cretaceous; *4* — the Paleocene — Eocene; *5* — the Oligocene — Lower Miocene (Maikop Series); *6* — the Neogene; *7* — Quaternary deposits; *8* — disjunctive dislocations; *9* — disjunctive dislocations controlling mineralization. Deposits and ore shows: I — Chiatura deposit, II—III — Kviril depression, IV — Megreli depression, V—X — Racha-Lechkhum depression, XI—XV — Shkmeri-Meleshursk group. *a* — manganese, *b* — phosphorites, *c* — glauconites and glauconitic sandstones, *d* — silicites.

All the deposits and shows of these minerals are associated with a horizon of siliceous-zeolitic tuffs and tuffites *(Fig. 2)*, in which zeolite is represented by clinoptilolite and silica — by opal, frequently recrystallized into chalcedony [MAKHARADZE, 1972].

Manganese, iron and phosporus are localized in the bottom part of the horizon and form an ore subhorizon, the structure of which varies in different exposures *(Fig. 1)*. The Chiatura deposit is monomineralic — manganese; shows in Racha-Lechkhum depression — bimetallic: iron and manganese; of a bimetallic nature is also a deposit in the axial zone of Kviril depression, changing into a monometallic (manganese) on the northern flank in the coastal stretch. In Megreli and in some parts of Racha-Lechkhum depression the ore subhorizon is represented by iron mineralization exclusively or is absent. Manganese is represented by oxides, hydroxides and carbonates, whereas iron — by glauconite, more rarely by hematite and hydrohematite. Phosphorites represented by francolite and collophane act in the ore subhorizon as cement for glauconites and glauconitic tuffs or tuffites forming also separate nodules with abundant inclusion of glauconite. In Chiatura deposit, contrary to other regions, phosphorites not containing glauconite form an independent parting of a nodular structure with a maximum thickness of 15 cm; it underlies the ore subhorizon along the so-called Main Fault that limits the deposit from the south-west. Here a barite mineralization is also recorded acting as a cement of phosphorites.

Silicites occur mostly in the middle part of the horizon of siliceous-zeolitic tuffs and tuffites, while their separate bands can also be found in the ore subhorizon. Silicites are represented by spongolites and opalolites, in which the content of pyroclastic and terrigenous material, opal, clinoptilolite and montmorillonite formed through the replacement of vitric ash varies within a wide range. The carbonate substance of silicites is mostly represented by dolomite and is present in a comparatively small amount; in Chiatura deposit it is completely absent.

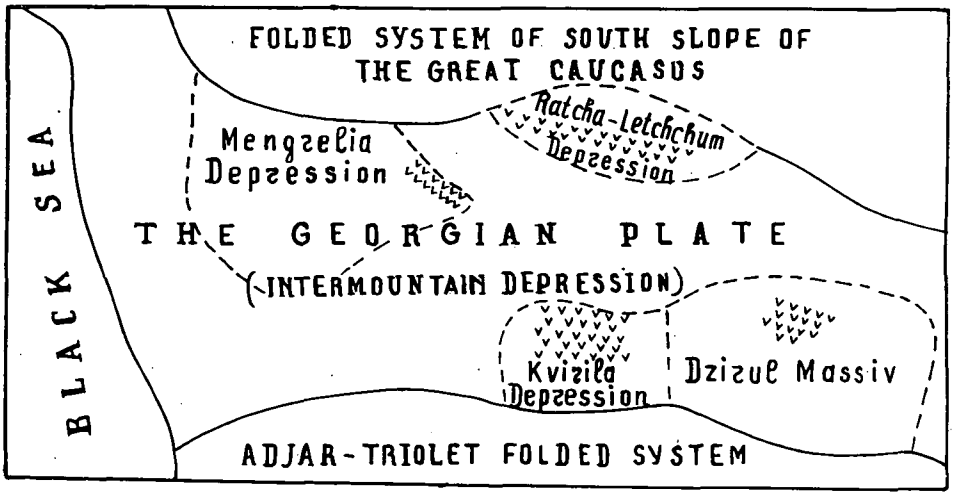

Fig. 2. Distribution scheme of the horizon of siliceous-zeolitic tuffs and tuffites of Lower Oligocene age on the territory of Western Georgia.

Fullest information and abundant material on the genesis of the minerals mentioned is accumulated for the Chiatura manganese deposit. The sedimentary origin of Chiatura deposit leaves no doubts, but there is no single opinion on its source. The available factual material indicates that Mn and the accompanying Si, Fe and P are not terrigenous, but are supplied by hydrothermal solutions and exhalations, as has been shown by G. S. DZOTSENIDZE [1969].

In Lower Oligocene manganese deposits and shows the accumulation of not only Mn, but also of Si, Fe and P is not being controlled by the mineral and granulometric composition of the terrigenous material, its influence being reflected only in its diluting effect. Both in the ore subhorizon and in the horizon of siliceous-zeolitic tuffs and tuffites, the terrigenous material varies by its mineral composition in different regions. In Dzirulsk massif, for instance, the terrigenous complex is characterized by a quartz-arkose composition, in Kviril depression it has an admixture of graywacke material. In Megreli and Racha-Lechkhum depressions the terrigenous complex is arkose-graywacke-quartzose. The accumulation of silica, manganese, iron, phosphorus and the formation of zeolite becomes superimposed on different rocks: sandstones, siltstones, clays, marls and limestones.

The above-mentioned lack of uniformity in the nature of structure of individual deposits and shows as well as the Mn, Si, Fe, P and Ba association are typical for a volcano-sedimantary type of deposits and alien to terrigenous-sedimentary types. The complicated pattern of interrelations between Mn, Si, Fe, P and Ba in separate Lower Oligocene deposits and shows can not be explained by the sequence of their evacuation from the crust of weathering according to the scheme of N. A. LISITZYNA [1968] or by the laws of normal sedimentary processes formulated by N. M. STRAKHOV [1963]. Elements belonging to different groups of the mobility series are found in a close association and against a uniform facies background produce maximum accumulations. The evacuation sequence of individual components in a sediment does not coincide with the sequence of their removal from the crust of weathering. At Chiatura deposit, for instance, the manganese ore process is preceeded by an accumulation of phosphates with barite. In deposits and shows of a bimetallic type iron though having lower mobility than manganese, is in a close association with the latter. In the shows of Racha-Lechkhum depression ferruginous bands alternate with manganese-bearing, while carbonate manganese ores contain inclusions of glauconite. In Kviril depression iron has maximum accumulations not in the coastal, but in the deeper part of the basin, where it forms both independent bands of glauconite, hematite and hydrohematite underlying and intercalating with manganese, and iron-manganese oolites.

One of the main proofs of a volcanic accumulation of Mn, Si, Fe and P serves their association with the horizon of siliceous-zeolitic tuffs and tuffites.

Very important is the question on the location of the sources of the ore substance and on the ways by means of which it is supplied to the basin.

There is a distincly expressed regularity in the spatial distribution of Lower Oligocene deposits and shows of Mn, Si, Fe and P that sheds light on the location of sources of the ore substances and on the ways of their supply to the basin. All the Lower Oligocene deposits and shows of Mn, Si, Fe and P are associated with disjunctive dislocations exclusively *(Fig. 1)*. The farther from these dislocations the more such deposits peter out, all the fundamental structure features of the ore subhorizon being controlled by the disjunctive dislocations. So, for instance, the Main Fault passes in the extreme south-western part of Chiatura deposit and along

this fault: *1)* the manganese ore subhorizon is characterized by its mass and an absence or least quantity of non-ore bands; *2)* silicites are most abundant, becoming more and more replaced by clays with an increase in the distance from the fault; *3)* the thickness of hydrothermally-altered ore is greatest, decreasing and petering out in getting farther away from the fault; *4)* the content of nickel, copper and cobalt in the ore is at its maximum; *5)* phosphorites and barite form maximum accumulations, barite being strontium-bearing.

The Main Fault represents a fracture of a deep-seated type that originated during a pre-Oligocene time, at the end of the Lower or in the beginning of the Middle Miocene it has been subjected to a rejuvenation. Along the plane of the Main Fault there are alterations in carbonate rocks expressed in a dolomitization of limestones, in their replacement by iron, manganese and a leaching resulting in the formation of cavernous textures.

Alterations along the disjunctive dislocations are also observed in the deposits underlying the horizons of siliceous-zeolitic tuffs and tuffites in Megreli and the north-western part of Kviril depressions. Paleocene-Eocene limestones and marle are dolomitized here and silicified; the width of the alteration zone comes to ths first several tens of meters.

In Kviril depression the main source of the ore substance has been located in its west-south-western part, which is indicated in this part of the depression by: *1)* maximum thicknesses of the ore subhorizon and of the silicites; *2)* maximum accumulations of iron in the form of glauconite, hematite and hydrohematite in amounts not below and sometimes exceeding the amounts of manganese *3)* maximum accumulations of phosphorus; *4)* the most rudaceous composition of the pyroclastic material.

Consequently, disjunctive dislocations served as incurrent channels for hydrothermal solutions; apparently, these dislocations were mostly distant from the centres of explosive volcanism, inasmuch as there are no traces of eruption centres anywhere near the places of a maximum accumulation of the ore matter.

The ore matter brought into the basin by the hydrothermae, as indicated by E. A. Sokolova [1968], precipitates as an ordinary mechanical suspension, the place of its precipitation being, to a great extent, determined by physico-geographical conditions and the laws of an ordinary terrigenous sedimentation.

In the Oligocene basin on the territory of Georgia islands that formed the archipelago had dissected coastlines and bays with an uneven floor relief characteristic for a littoral shallow sea. These bays represented traps for the finely dispersed ore matter. The ore suspension was drifted by the currents all over the bay and got buried in places of a weaker hydrodynamic regime — in the hollows of the floor. The morphology of the latter determined the lenticular-bedded texture of the ore subhorizon. At a distance from the source the ore suspension gradually became dispersed in the water.

A most favourable combination of the location of the ore matter source with the paleogeographical environments is recorded for the Chiatura deposit. A maximum accumulation of ore components in the south-western part of the deposit resulted from a direct proximity of the ore matter source and from the paleogeographic environments. In this part of the deposit, despite the neareness of the coastline the supply of terrigenous material and its diluting effect on the ore matter has been small during the time when hydrothermal solutions penetrated into the basin. Such a situation has been determined by the following factors: owing to an intensification

of the Oligocene transgression in a south-western direction, the level of erosion was gradually rising and the supply of material from the land constantly diminished; this material has been in a finely dispersed state; limestones, which formed the bulk of the denuded land in the south-western part of the basin, contained small amounts of an unsoluble residue; the narrow isthmus that separated the basin from the Kviril depression did not contribute to the development of abundant rivers that could supply large amounts of terrigenous material.

Among the favourable factors that contributed to the formation of Chiatura deposit mention should be made of the physical properties of rocks through which the metalliferous solutions migrated. The Main Fault dissects crystalline rocks of Dzirulsk massif and the overlying limestones. These rocks are very dense so that the circulating metalliferous solutions are hardly absorbed [DZOTSENIDZE, 1969]. It might be that the comparatively small sizes of ore shows in the Racha-Lechkhum depression and adjacent areas are, to a certain extent, determined by the fact that Middle Bajocian volcanic rocks participating in their structure absorbed a substantial part of the metalliferous solutions letting through to the surface only their small portions.

The first portions of hydrothermal solutions supplied to the Chiatura basin contained Ba, P and Sr. Barium rapidly entered into a reaction with the sulphate-ions of the sea water entrapping part of the strontium and precipitated near the point of issue of the solutions. An intense precipitation of phosphorus was also taking place along the Main Fault, where this element had high concentrations. At a distance from the source phosphorus became rapidly diluted by sea water. The subsequent portions of hydrothermal solutions contained a great amount of manganese. The location of the source of the ore matter in the south-western coastal zone with a well aerated floor determined the oxidation of the Mn^{2+} supplied by the hydrothermal solutions into Mn^{4+} and the formation of pyrolusite-psilomelane ores near the source. Owing to the scarcity of bios in the coastal stretch and a low generation of organic matter by the intensely precipitating manganese hydroxides, the reduction of Mn^{4+} into Mn^{2+} during a diagenesis had been of no substantial importance. The farther from the source in a north-eastern direction, in the abyssal part of the bay, where oxygen is less active, the intensity of the oxidation process and the alteration of Mn^{2+} into Mn^{4+} weakens, and the accumulating amounts of organic matter contribute to a reduction of the oxidized forms of manganese. The pyrolusite-psylomelane ores occurring in the south-western part of Chiatura basin, are gradually replaced in the north-east through manganite ores by carbonate varieties. The overlapping of oxide ores by carbonate ores in the vertical section can be explained by a widening and deepening of the basin and a shifting of the coast line to the south-west.

In Kviril depression, contrary to the Chiatura deposit, hydrothermal solutions contained a substantial amount of iron, which determined the bimetallic nature of the deposit its source having been located in the deep central part of the basin. Near the source iron precipitated as glauconite, more rarely as hematite and hydrohematite and manganese — as manganite and carbonates; there has also been a precipitation here of phosphorites. Manganese could also migrate and get deposited in more distant parts of the basin than the iron, like the coastal stretch of the northern flank of Kviril depression forming pyrolusite-psilomelane ores.

In the Racha-Lechkhum depression the ore matter has been deposited on a basin floor with a highly reduction medium, which determined an exclusive formation of carbonate manganese ores.

In this way, the source of Mn, as well as of the accompanying Si, Fe and P in Lower Oligocene deposits and ore shows consisted in hydrothermal solutions, for which disjunctive dislocations served as incurrent canals. Some deposits and shows had independent sources of supply that differed by the composition of individual components, which determined a varied nature of their structure. The structure, mineral composition and size of Lower Oligocene deposits and shows o manganese, silicite, phosphorites and iron depends not only upon the composition and amount of ore matter supplied by the hydrothermal solutions; an important role belongs also to paleogeographic conditions, the morphology of the basin floor, the hydrodynamic and hydrochemical regime of the basin, the location in it of the source of the ore matter, the physical properties of rocks along which the metalliferous solutions have been migrating.

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STUDY OF MONGHOPIR SPRING WATERS

K. A. MALLICK and I. A. K. AFRIDI

ABSTRACT

The present investigation of the waters of the hot and warm springs of Monghopir area in Karachi County, Sind, shows that they are significantly different in their physical properties and chemical composition.

Geochemical behaviour of the chemical constituents of the waters have been discussed. Possible causes of changes in chemical composition of waters have also been described.

INTRODUCTION

Reference to the occurrence of thermal springs in Indo-Pakistan subcontinent is found in many reports of the last century. A summary of information on the occurrence of thermal springs of this subcontinent was published by MACPHERSON [1854] and later on by SCHLAGINTWEIT [1864]. OLDHAM [1882] also published a catalogue of the hot springs known at that time. GHOSH read his presidential address on the thermal springs of Indo-Pakistan subcontinent in the Indian Science Congress held in 1950. Later works of the officers of the Geological Survey of Pakistan added informations on the occurrence of thermal springs in Pakistan.

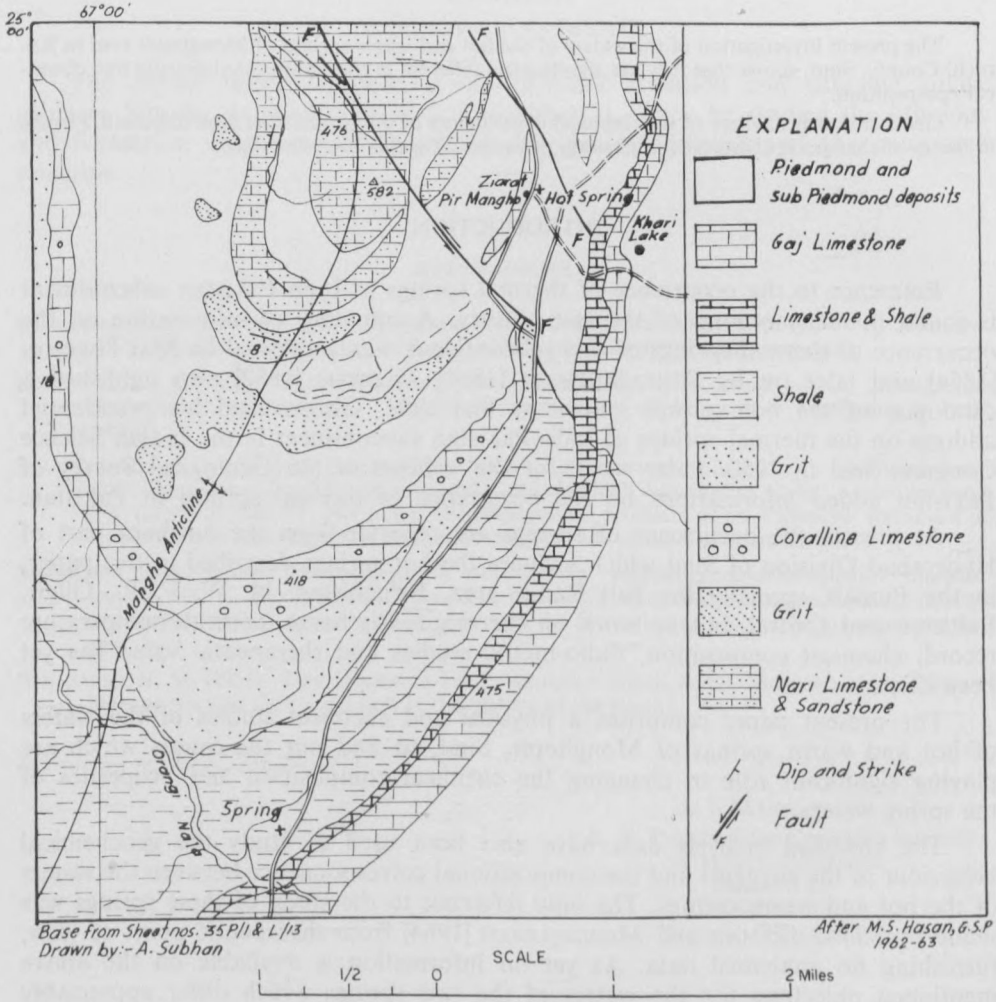
At present the occurrence of springs are reportes from the northern part of Hyderabad Division of Sind which includes the hot springs described in this paper, in the Punjab, specially the Salt Range area, Baluchistan, N. W. F. P., Gilgit, Baltistan and Chitral, but no work on the origin, discharge, accurate temperature record, chemical composition, radio-metric studies and therapeutic value has yet been done.

The present paper comprises a physical and chemical studies of the waters of hot and warm springs of Monghopir, Sind, to find out the causes which are playing significant role in changing the chemical composition and properties of the spring waters.

The chemical analysis data have also been used to study the geochemical behaviour of the elements and the compositional correspondence between the waters of the hot and warm springs. The only reference to the study of these springs was made by RAFIQUZZAMAN and MEHDIHUSSAN [1964] from therapeutic point of view, furnishing no analytical data. As yet no information is available on the above mentioned objectives for the waters of the two springs which differ appreciably from the other cold springs of the region. This attempt is first of its kind.

The hot and warm springs of Monghopir are situeted in Karachi county, at a distance of about 15 miles north of Karachi University. The distance between the two springs is about two furlongs and both are oozing out along the fault plains in Gaj Limestone. Apparently these springs differ in their temperature and the amount of hydrogen sulphide and carbon dioxide evolution which come out on the surface in the form of bubbles.

Besides the hot springs in Monghopir village there are quite a number of springs in the locality such as Khari Lakki, Ziarat and Lal Chakro etc, but they do not posses similar properties as mentioned above for the hot and warm springs. On the contrary the water of Lal Chakro spring is used for drinking purpose by the local inhabitants.



GEOLOGICAL MAP OF MANGHO PIR AREA

Fig. 1

The rocks exposed in the area of Monghopir are Nari, Gaj and Manchat formations of Oligocene, Miocene and Pliocene ages respectively *(Fig. 1)*. Nari Formation is mainly composed of sandstone, limestone and shales. The sandstone is medium to coarse grained in general but gretty character and iron concretion can also be seen in the sandstone bed. The cementing material is argillaceous to ferro-argillaceous which weathers to brown, rusty brown, yellow and dark grey from its original grey and light brown colour. The sandstone is loose, friable and highly porous. Horizontal and vertical joints are common.

The brown Nari shale is found interbedded with the limestone and the sandstone. The abnormal thickness of the shale varies from 256 to 335 feet but thin layers appearing as parting between the two beds of the limestone and the sandstone are also common. Iron concretions are rare in the shale, but gypsum is commonly found. The colour is generally grey but red, green, yellow and variegated colours also be seen.

The fossiliferous limestone is found above the Nari sandstone, in five different beds alternating with the sandstone and shale layers. Joints are less developed in the lower most bed of the limestone but the upper beds are appreciably jointed. The chemical analysis shows the dominance of silica and argillaceous matter, besides a high percentage of calcium carbonate. The topmost bed of Nari Limestone is highly fossiliferous. Among the fossils, forams and corals are the dominant indicators of life at the time of deposition of Nari Formation.

Coralline limestone of cream colour stands out between the top of Nari Formation and the base of the Gaj Formation. The age of this limestone is still a matter of dispute.

GAJ FORMATION

Gaj Formation comprises of limestone, shale and sandstone in order of their abundance. The total thickness of the formation is 1300 feet. The limestone is argillaceous and porous but hard and resistant to weathering to a great extent. Fossils are abundant in this limestone and at some places it appears to be formed of shells and tests only. Cavity formation and presence of horizontal and vertical joints are common features of this limestone.

The shale is gypsiferous and grey in colour. It is soft, fine grained and loose in texture. The shale is found alternating with the grey sandstone.

The grains of the sandstone are moderately rounded and medium in size. The texture of the sandstone is loose due to argillaceous cement. Iron concretions are common.

Cracks and joints developed in the limestones and sandstones are numerous and are widened as a result of solution action. These craks and joints enhance the effective permeability in the sandstone and limestone for ground water accumulation in the area.

PHYSICAL PROPERTIES OF THE SPRING WATERS

In Monghopir the spring sites are about 582 ft above sea level. Though the distance between the two springs described is about two furlongs but the hot spring gives a discharge of about 1200 gallons of sulphurated water per day as compared to the warm spring which discharges only 500 gallons of water in a day (KDA report 1963) and no smell of sulphurated hydrogen gas is felt in it.

Besides the prominent difference in the quantity of discharge of waters from the hot and warm springs and the dissolved gasses in them, they also show an appreciable difference in their hardness, electrical conductivity, pH condition and turbidity of water (Table 1). Specific gravity, surface tension and viscosity, the refractive index of the water also show some differences but these properties are not as distinctive as the other characters determined for the present work.

TABLE 1

Physical properties

No.	Characteristics	Hot spring	Warm spring
1.	Colour	Under 0.5	Lovibond unit yellow
2.	Odour	Smell of H_2S	None
3.	Taste	Slightly Saltish	Slightly Saltish
4.	Temperature	47 °C	38 °C
5.	Turbidity	0.5	0.1
6.	Specific Gravity	1.0016	1.0019
7.	Surface tension	71.77	70.95
8.	Viscosity at 31.5 °C	0.00782	0.00781
9.	Electrical Conductivity at 35 °C	0.00286	0.00350
10.	Refractive Index	1.3328	1.3327
11.	Permanent Hardness	31.5 ppm	56.4 ppm
12.	Total Hardness	271.5 ppm	371.5 ppm

GEOCHEMICAL STUDY

Standard classical chemical analysis methods were used for the quantitative analysis of major and important minor components of the waters collected from the hot and warm springs.

The result of chemical analysis shows a marked antipathic trend of enrichment and depletions for Ca and K in the waters of hot and warm springs. The concentration of calcium is very high (88,88 ppm) in warm waters as compared to the hot water which contains only 26,28 ppm, but reverse is true for the concentrations of potassium (Table 2).

The concentration of magnesium is relatively higher in hot water than the warm water of the spring (Table 2). There is not much difference in the iron content of the two waters.

The content of sulphate, nitrate, consumed oxygen, albuminoid ammonia and evaporites are significantly higher in warm water than in the hot water, but reverse is true for the concentration of free ammonia and hydrogen sulphide which is practically absent in warm water.

TABLE 2

Chemical properties

No.	Characteristics	Hot spring (ppm)	Warm spring (ppm)
1.	Hydrogen sulphide	0.034	Nil
2.	Nitrite	0.002	0.001
3.	Nitrate	0.320	0.369
4.	Chloride	424.00	600.00
5.	Sulphate	217.51	336.69
6.	Phosphate	Nil	Nil
7.	Silicate	(in traces)	(in traces)
8.	Alkalinity	240.0	315.0
9.	Consumed Oxygen	0.15	0.2
10.	Free ammonia	0.024	0.004
11.	Albuminioid ammonia	0.052	0.084
12.	Calcium	26.28	88.88
13.	Magnesium	34.52	28.93
14.	Potassium	24.80	14.56
15.	Iron	0.12	0.10
16.	Evaporates (qt 120 °C)	1394	1752
17.	pH	8.20	7.2

Silica was found in traces only in hot water. Phosphate content was not found in either of the water samples.

The water samples of both springs are alkaline, but the sample of warm spring shows more alkalinity as compared to the hot spring water.

DISCUSSION

If it is assumed that there is an average increase in temperature of 1 °F at every 100 ft of depth below the surface of the earth then the temperatures of the hot (140 °F) and warm (126 °F) springs show a depth of about 1400 and 1260 feet respectively for the source of waters. The calculated values of depth do not give the correct depth of the source, because some of the heat energy is also being dissipated in the channels and in the rocks through which they pass. The loss and gain of heat due to exothermic and endothermic reactions at the source or in the channel is also not beyond possibilities.

Thus it seems fair enough to conclude that the temperature of waters of the two springs are not related only to the depth of the source of waters, but the reasons mentioned above are also playing significant role.

The difference in chemical composition of waters of the springs seem related more to the temperature conditions than to the depth and the area of catchments of the two springs.

The great difference in discharge of water of the hot (1200 gallons/day) and warm (500 gallons/day) springs may be due to the difference in extent of catchment areas or some subsurface flow of water may be connected to the channel of the hot spring.

The absence of hydrogen sulphide in the warm spring and the presence only in the hot spring (0,034 ppm) is either due to dissolution of gypsum from gypseous shale of Nari age in the hot water coming from inside or the hot water is passing through such a channel of rocks which contains sulphides or sulphates. The decomposition of sulphides or sulphates may the source of hydrogen sulphide gas but the chances are very remote due to absence of any sulphide deposits in this region. It is true that under normal conditions, hydrogen sulphide is not formed at higher pH values, but in nature specially in the subsurface where temperature and pressure are higher and physico-chemical conditions are complex, the acidic water after reacting with the sulphates or sulphides would have proceeded upward on way to the mouth of the springs with changes towards slightly alkaline state (8.2). Relatively higher content of consumed oxygen in warm spring is an other support to the arguments given above. The lower content of sulphate in the hot (217,51 ppm) as compared to the warm (336,69) spring also favours the present statement. The possibility of formation of hydrogen sulphide through the reaction between sulphates and organic acids formed due to the decomposition of organic matter can not be neglected. A secondary channel for the supply of hydrogen sulphide may also be considered as one of the causes.

Higher percentage of calcium in the warm spring (88,88 ppm) as compared to the hot spring (26,28 ppm) does not favour the possibilities of formation and concentration of H_2S simply due to the decomposition of gypsum. Magnesium appears to be in antipathic relationship with calcium. The trend of enrichment and depletion for K is the same as for magnesium.

The antipathic relationship of Ca & Mg does not seem completely in accordance with ATKINS [1939] observations who explains that Mg is readily soluble above pH 9 while calcium precipitates above a pH value of 11. The present observation shows that even at lower pH values of 7 to 8 the solubility of magnesium and calcium is affected if higher temperature condition is attained. The trend of K in the two springs following the concentration of Mg is due to its higher affinity with magnesium [RANKAMA & SAHAMA p. 431—34].

The absence of phosphorous in the two waters shows that no minerals or fossils containing phosphorous are present at the source of the waters and in the channels through which they pass. The observation also gets support from the known fossils of Nari and Gaj limestones of the area which contain mainly calcium carbonates in their chemical composition.

The presence of silica only in traces in the waters of the springs passing through argillaceous limestone and sandstones indicate acidic condition of waters. It could also be possible that waters at the source are incompetent to dissolve such constituent which require higher alkalinity to decompose the minerals or rocks.

Relatively higher amount of nitrates in warm water as compared to the hot water of the springs also seems to be sensitive to the alkalinity of the water.

The presence of higher amount of sulphate in warm spring could have been due to the decomposition of the gypsum.

The formation of sulphate seems sensitive enough to the chemical conditions and so the amount of sulphate is less in hot spring which has relatively higher alkalinity (8.2).

Chlorides show the same tendency of enrichment and depletion as the sulphates. It appears that the concentration of sulphate, nitrate and chloride is favoured in neutral to slightly alkaline chemical environment.

MACPHERSON [1854] states that probably the hot spring water of Monghopir is arsenical and so it is used for the remedy of skin deseases.

The chemical analysis of the water for present study does not show the presence of arsenic within the detection limits in waters of the hot and warm springs of this region. MACPHERSON's statement seems to be hypothetical as he did not make any chemical analysis of the waters. Moreover, he did not consider that sulphur in different states is also used as good insecticides. Therefore, it is possible that the remedy of skin deseases for which the waters are being used is due to the presence of sulphur in different forms and not the arsenic.

ACKNOWLEDGEMENT

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ORTHOPYROXENES FROM SUKINDA ULTRAMAFITES AND THE NATURE OF THE PARENTAL MAGMA

SACHINATH MITRA

ABSTRACT

Chromite-bearing ultramafites occur as synkinematic intrusions during the Eastern Ghat orogenic movement (2800—3000 m. y.), in Eastern India. The ultramafic instrusives are composed mainly of dunite, bronzitites, websterite and their metamorphic derivatives. These were emplaced by successive 'pulsation' intrusions and show some layered features.

Pure (>99,9%) orthopyroxenes separated from bronzitite, peridotite, websterite etc. were analysed by Philips automatic PW 1212 X-ray fluorescence spectrometer. The analyses revealed very low Al and Ca content compared to most other widely known localities of layered types. The En values (80—83%) are also lower than those of many alpine and stratiform complexes.

The crystallochemical considerations of the orthopyroxenes lead the author to assume a peridotite primary magma rather than a basic magma, occurring below the substratum in the Eastern Ghat region of E. India. To account for the crystallization of monomineralic rocks such as dunite, enstatitite, chromitites etc., liquids of these rock compositions are assumed to have been locally produced by partial fusion of peridotites. Absence of any literature in this direction leads the author to presume that Sukinda magma was compositionally unlike any of the presently known uppermantle magma genetic zones. The intrusive magma, however, might be contaminated during orogeny to change the path of crystallization.

INTRODUCTION

An ultramafic complex of Sukinda lying between Saruabil and Kolrangi (21°0′—21°5′ N:85°33′ E) occurs as syn-orogenic intrusions in the Iron Ore Series formations of the Eastern Ghat region. The intrusions took place during the Eastern Ghat Cycle 2800—3000 m.y. [SARKAR, 1968] ranging in the period Mesarchean to Katarchean [RAO, 1967].

The part of the complex studied covers an area of about 60 sq. miles and is composed mainly of perioditite, harzburgite, enstatite (with bronzitite), websterite, dunite, and their metamorphic equivalents, the details of which are treated elsewhere [MITRA, 1959, 1961]. The petrology and the mechanics of emplacement of the intrusives were first described by the author [1960] followed by CHATTERJEE and BANERJEE [1964]. The former considered the complex as a multiple intrusion with two major phases of intrusions of ultramafic magma, emplacing rocks and chromites from different horizons of a fractionated magma. The ultramafic intrusions were followed by basic and late acidic intrusions such as granophyre, granite etc. The latter are proved at depth by bore holes at the southwestern part of the map *(Fig. 1)*.

The ultrabasic intrusives trend NE—SW along the valley between the two quartzite ridges of Iron Ore Series, exposed in the north (the Daiteri range) and the south (the Mahagiri range) of the area (see the map, *Fig. 1*).

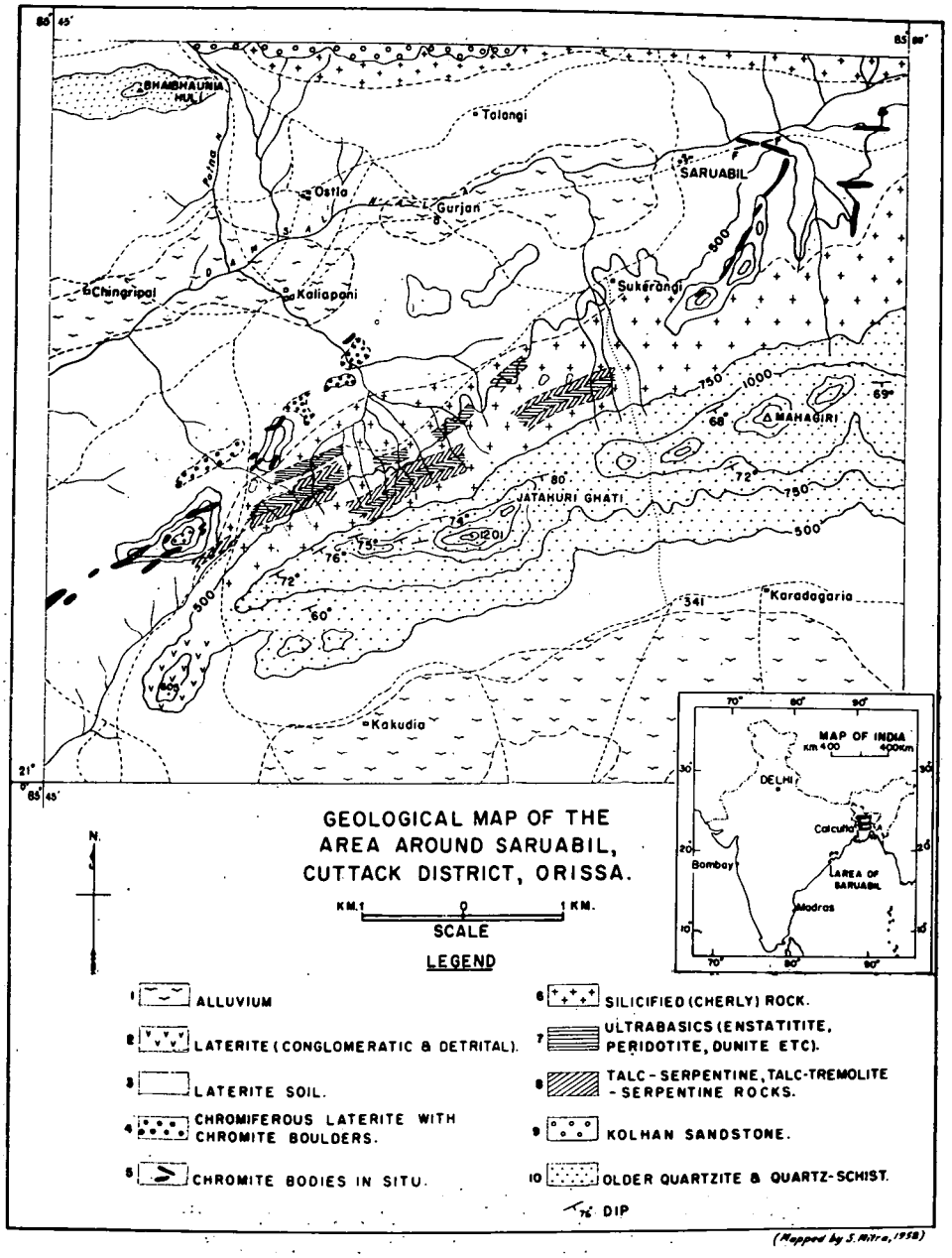

Fig. 1. Geological map of the Sukinda area around Saruabil and Tomka, Cuttack district, Orissa, India.

Fig. 2a. A photograph of a chromite quarry showing the layered nature.

The ultrabasic and the chromitites carry incipient to conspicuously layered structures formed by crystal settling and accumulation, also these are superimposed by tectonic layers. The earlier intrusive, exposed to-day exclusively as chromitite band at the village Saruabil (21°3′13″:85°35′) show such layering distinctly *(Fig. 2)*.

Extensive serpentinization, steatization and silicification removed all identifying traces of the ultramafic rocks associated with these chromite layers. At a later period intrusives of websterite, harzburgite, enstatitite, dunite and chromitite came up along the flanks of a syncline formed during Eastern Ghat Orogeny. Some of these rocks, occurring in the southern flank of the syncline are exposed near the

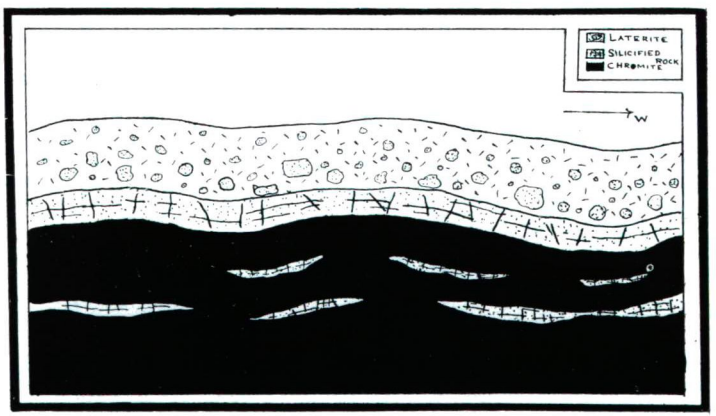

Fig. 2b. A diagrammatic representation of the E-W sectional view of the chromite lode of Q4 (S. C. M). The silicified bands of ultrabasic in chromite suggest its stratiform nature.

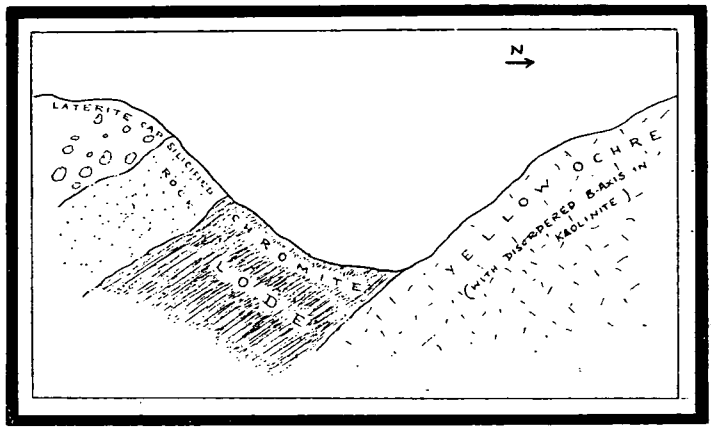

Fig. 2c. N-S section of the same as that of Fig. 2b.

foot-hills of the Mahagiri, which is found to be the zone of high pressure and shearing stress [MITRA, 1970].

Detailed petrographic and mineralogical investigations were carried out by the author since 1958 and individual mineralogical investigations have been taken up during the last four years to determine the mineralogical criteria for deciphering the nature of the present magma, and also to ascertain the process of crystallization and the mechanism of emplacement. In recent years, mineralogical criteria have been used in deciphering whether an intrusive is an Alpine Type or Stratiform Type [HESS, 1955, 1960; THAYER, 1960] or intermediate type having characters of both. Author's investigation on olivines from the present area [MITRA, 1970] indicated a magma of Alpine-type peridotite.

In the present paper the author has attempted to estimate the implications of the composition of orthopyroxenes of the enstatitites (bronzitites) and websterite collected from the southern part of the area.

MAJOR OXIDE ANALYSIS

Five samples of orthopyroxenes collected (hand picked under binocular microscope) from Sukinda enstatite and websterite were analyzed by using a Philips 1212 automatic X-ray Fluorescence Spectrometer. Major and trace elements were analyzed from prepared briquettes. (The counts were corrected for absorption and matrix by using the technique and computer programme of HOLLAND and BRINDLE, 1966*). The data are present in Table 1.

Calculations of the molecular percent of En [En = 100 Mg/Mg + Fe (total) + Mn] shows a variation from 80,38 to 83,30 (Table 2). The orthopyroxenes are biaxial positive and according to the nomenclature of DEER, HOWIE and ZUSSMAN [1963, 2, p. 9] these are enstatites. Some, however, place the boundary between enstatite

* All iron counts in the scintillation counter were originally calculated as Fe_2O_3 according ot the programme used. The Fe_2O_3 were calculated to FeO and the total was recalculated to proximate 100.

TABLE 1

Chemical analyses of orthopyroxenes from Sukinda ultramafites

Serial No.	1	2	3	4	5
Sample No.:	Ex	B124	B123	B68	M434
SiO_2	57.00	56.38	57.23	57.08	56.55
Al_2O_3	0.78	0.78	0.80	0.66	1.03
FeO	5.81	5.78	5.75	5.96	6.60
MgO	35.73	36.57	35.54	35.75	34.96
CaO	0.65	0.43	0.64	0.49	0.77
Na_2O	0.001	trace	0.01	0.04	0.02
K_2O	0.03	0.03	0.03	0.03	0.07
TiO_2	trace	0.03	0.03	0.03	0.001

and bronzite at En_{90} Fs_{10} [POLDERVAART, 1974]. According to that, therefore, these orthopyroxenes (En 80—83 Fs 20—17) from Sukinda are bronzite. In Table 6, these orthopyroxenes are compared with those from other areas with respect to their En values.

The compositions of these pyroxenes are studied in the light of the atomic and crystal chemistry to evaluate the stability range, temperature of formation and the nature of parental magma from which these pyroxenes crystallized.

TABLE 2

Cation percentage of Sukinda orthopyroxenes

Serial No.	1	2	3	4	5
Sample No.:	Ex	B124	B123	B68	M434
Si^{+4}	49.62	49.23	57.79	57.66	48.98
Al^{+3}	0.88	0.60	0.74	0.62	1.35
Fe° (Total)	8.42	8.32	7.02	7.27	9.52
Mg^{+2}	40.17	41.23	33.67	33.83	39.05
Ca^{+2}	0.86	0.58	0.73	0.55	1.01
Na^{+1}	trace	trace	0.02	0.05	0.02
K^{+1}	0.04	0.04	0.03	0.03	0.11
Ti^{+4}	trace	trace	trace	trace	trace
Total	100.00	100.00	100.00	100.00	100.00
En ratio:	82.83	83.20	82.74	82.31	80.38

A comparison of the lime contents of Sukinda ultramafites with those of Ca-poor pyroxenes from basaltic parent magma and ultramafic 'magmas' as given by HESS [1960, p. 32, Table 5] is made in Table 3.

TABLE 3

CaO content in the orthopyroxenes of different parentage

	Average CaO (wt %)	Range CaO (wt %)
Orthopyroxene (Sukinda)	0.60	0.43—0.76
Basaltic parentage inverted pigeonite or pigeonite	0.31	3.8 —5.1
Ultramafic parentage orthopyroxenes	0.9	0.2 —1.9

Orthopyroxenes from nodules and intrusive peridotites are considered to be low in Ca and are derived from Ca-deficient magma [HESS, op. cit.]. HESS gave a range of 1,35—1,93% CaO for pyroxene derived from basaltic magma and 0,23—1,95% CaO for those from ultramafic magma. Table 3 shows the affinity of the Sukinda ultramafics to the latter source.

HESS later [1963] pointed out that although 'Ultramafic' orthopyroxenes usually have low lime contents, slightly higher values might be attained by fractional crystallization and early separation of Ca-deficient olivine, thus enriching the residual magma in lime. However, the orthopyroxenes from garnet — peridotites, quoted by O'HARA and MERCY [1963] are notably lime deficient.

The Ca-poor Sukinda orthopyroxenites indicate a peridotite magma source from which much less dunite fractions have been formed by crystallization fractionation than would be required for leaving a melt with greater amount of calcium for the formation of Ca-rich orthopyroxene and clinopyroxene exsolutions. Dunites, indeed occur only as a few minor bodies in this region. The orthopyroxenites cover far greater area than dunites. The proportions of spatial distribution of these two rocks have not, however, been determined by the author. The Ca-deficiency in orthopyroxenes, however, indicates that these pyroxenes were formed in a slow cooling condition, as otherwise, Ca-rich phases would form in a rapidly cooling stage.

ATLAS [1952] in a study of the synthetic system $MgSiO_3$—$CaMgSi_2O_3$ found that the amount of lime in enstatite varies with temperature as in Table 4.

TABLE 4

Ca atoms in enstatites and the temperature of formation

T°C	Number of Ca atoms (per unit cell) on the basis of 6 oxygens
1100°	0.115
1000°	0.050
700°	0.030

In the Sukinda enstatites the number of Ca-atoms per unit cell varies from 0,02 to 0,03 (rather 0,016 to 0,029, vide Table 8) suggesting a temperature range of about 700°C and below. No evidence of contact effect due to the intrusion could be seen in the area.

In Sukinda enstatites lime increases with alumina (except in B68) as also observed in Lizard [GREEN, 1963]. This suggests that temperature may partly control the entry of alumina into pyroxene structure.

MINOR OXIDE ANALYSES

Trace element and minor oxide content of the Sukinda orthopyroxenes determined by X-ray fluorescence are given in Table 5. Nickel, chromium and manganese are significantly higher in the relatively low alumina orthopyroxenes than in the high alumina ones. The range (in weight percent) of the minor oxides of the Sukinda

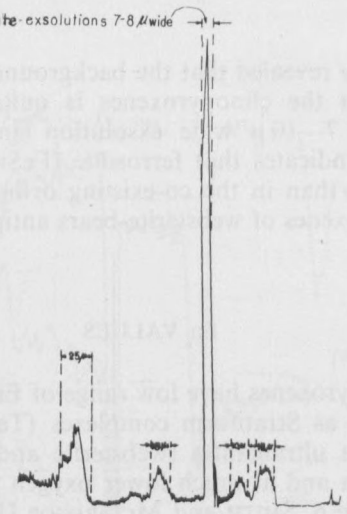

Fig. 3. Electron microprobe scanning for Cr over bronzite in enstatite.

enstatites are compared with those from other sources (Table 5) and it is found that these percentages cover a wide range but differ conclusively from those of the garnet — peridotite sources which contain notably less Cr_2O_3 and NiO. The orthopyroxenes from the garnet-peridotites, analyzed by O'HARA and MERCY [1963], were collected from Norway and the kimberlite pipes of South Africa. Other non-garnetiferous ultrabasic rocks occurring in the pipes contain slightly greater amount of Cr_2O_3 (0,2—0,6%). Pulverized samples of enstatite were also analyzed by the author for the estimation of trace mercury using the mercury vapour absorption meter at a set-up described by MITRA [1970]*. In the treatment 300 mA at the induction heater was used and the trace amount of mercury observed to range between 0,002 to 0,01 ppm (aprox.).

* This was done by the author when the instrument was handled by the author for the geochemical investigation for the base-metal mineralization between the two granites at Dartmoor and Bodminmoor) in SW England [MITRA and WEBB, 1967].

TABLE 5

Trace element content of Sukinda orthopyroxenes

	Cr_2O_3	TiO_2	MnO	NiO	References
Sukinda	0.04—0.8	0.001—0.2	0.01—0.1	0.1—0.25	Author
Lizard	0.4—0.7	0.2—0.4	0.1—0.2	n. d.	GREEN [1963]
Nodules	0.3—0.9	0.02—0.3	0.1—0.2	0.5—0.1	ROSS *et al.*, 1959.
Alpine type peridotites	0.6—0.8	0.02—0.2	0.1	0.1—0.2	ROSS *et al.*, 1959.
Garnet peridotite	0.02—0.2	0.05—0.1	0.1—0.2	0.003—0.005	O'HARA and MERCY, 1963.

Electron-probe study revealed that the background for chromium in the orthopyroxenes as well as in the clinopyroxenes is quite high. The orthopyroxenes (bronzites) show about 7—10 μ wide exsolution lamellae of chromite *(Fig. 3)*. Microprobe study also indicates that ferrosilite ($FeSiO_3$) molecules are more prevalent in clinopyroxenes than in the co-existing orthopyroxenes *(Fig. 4)*, although Fe in diopsidic clinopyroxenes of websterite bears antipathetic relation with calcium *(Fig. 5)*.

En VALUES

The Sukinda orthopyroxenes have low range of En values (80—83%) compared to many Alpine as well as Stratiform complexes (Table 6). These low En values suggest that the Sukinda ultramafites (websterite and enstatites) were crystallized in a nearly dry condition and at much lower oxygen pressure (partial) than in the other cases cited in Table 6. SMITH and MCGREGOR [1960] describe high En orthopyroxenes from the Mount Albert Complex as occurring in areas of high serpentinization and suggest that during crystallization increase in water pressure has

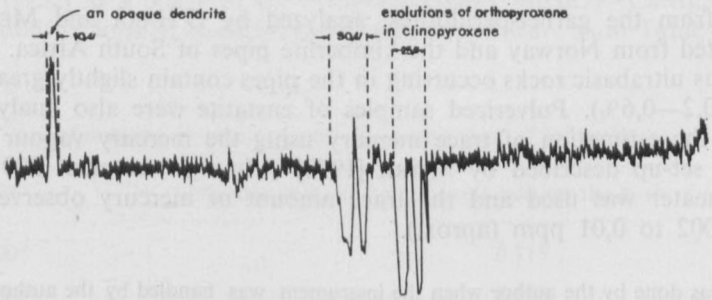

Fig. 4. Electron probe scanning for Fe over co-existing clinopyroxenes and orthopyroxenes.

increased partial oxygen pressure in these areas resulting in more Mg-rich orthopyroxenes. No evidence for increasing En in the serpentinized areas, in the southern region near the Mahagiri, could be traced by the author (analyses 4 and 5). The samples M 434 and B 68 were collected from the southwestern part of the map near Mahagiri, where serpentinized and schist bands occur in association with these ultrabasics. An analysis of the serpentinized pyroxenite (with relict grains of orthopyroxene; sample no. P 125, collected from 1 km. S. W. of Purnapani village) is presented in Table 7 on water free basis for comparison with those of orthopyroxenes of this area (Table 1). This evidently indicates that the serpentinized body represented by P 125 was enstatitites and was also formed at a low oxygen pressure. Unfortunately other samples of this locality could not be analyzed.

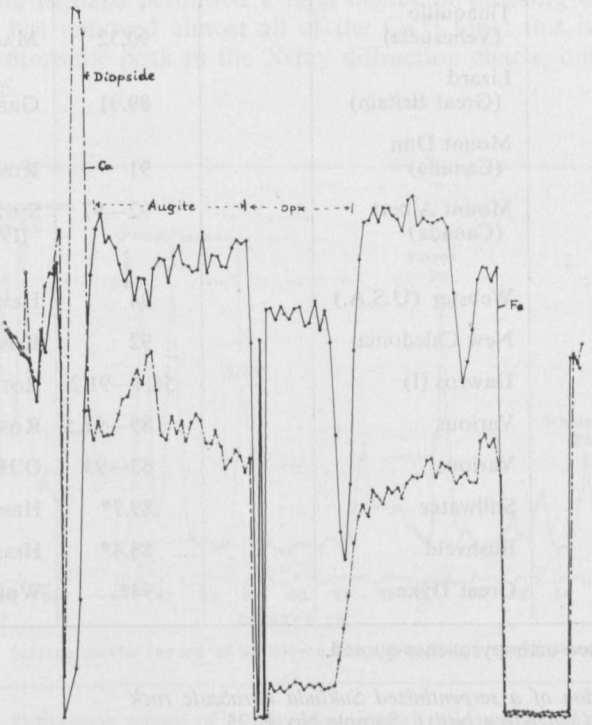

Fig. 5. Geoscan traverse for Ca and Fe over diopside with exsolved orthopyroxenes.

The serpentinization of the second phase intrusives, exposing in the SW part of the area was, indeed, later than the main period of intrusion [MITRA, 1960] and the magmatic change over to serpentine in this case were very incipient for consideration.

For comparison the Fe contents of olivines occurring in the associated rocks viz., harzburgite, peridotite, dunite, iddingsite rock (with olivine) and chilled gabbros, as already reported by the author elsewhere [MITRA, 1970], are presented in Table 6 along with those from other environments of the world. The Fe content of olivines varies between 81% to 93% in the ultramafites of the present area, corresponding to the En range of the orthopyroxenes 80—83%.

TABLE 6

Comparison of mol. per cent of En in orthopyroxenes from different regions

Type	Area	Sample No.	En value	References
	Sukinda Orissa	Ex	82.83	Author
		B124	83.20	
		B123	82.74	
		B68	82.31	
		M434	80.38	
Alpine	Tinaquillo (Venezuela)		90.32	MACKENZIE [1960]
	Lizard (Great Britain)		89.91	GREEN [1964]
	Mount Dun (Canada)		91	ROSS *et al.* [1954]
	Mount Albert (Canada)		92—97	SMITH and MCGREGOR [1960]
	Webster (U.S.A.)		94	HESS [1952]
	New Caledonia		92	ROSS *et al.* [1954]
	Dawros (I)		56.4—91.2	ROTHSTEIN [1958]
Nodules in Basalt	Various		89—91.5	ROSS *et al.* [1964]
Garnet peridotite	Various		83—93	O'HARA [1963]
	Stillwater		89.7*	HESS [1956]
Layered Complexes	Bushveld		88.4*	HESS [1952]
	Great Dyke		94*	WORST [1958]

* Earliest formed orthopyroxenes quoted.

TABLE 7

Composition of a serpentinized Sukinda ultrabasic rock (water-free basis) Sample No. P125

	SiO_2	56.01%
	Al_2O_3	0.55
(Total iron as)	Fe_2O_3	6.30
	MgO	36.68
	CaO	0.43
	Na_2O	Trace
	K_2O	0.03
	Total	100.00%

One important consideration of the other aspect of the enstatite compositions is their low alumina content, which is generally below 1%. Some cases, having $Al_2O_3 > 1\%$, however, led the author to postulate a possibility of formation of some isolated chemically heterogeneous pockets or lenses of nearing garnet-peridotite composition or some minor layers with higher Ca, Al and Fe content in the magma.

CRYSTAL CHEMISTRY

Investigations of the orthopyroxenes of this area reveal characteristics of slow cooling with nearly complete removal of Ca in diopsidic clinopyroxenes which occur occasionally as thin exsolution lamellae or as blebs.

Slow cooling perhaps permitted a high degree of ordering and the exsolution of the lamellae has removed almost all of the Ca^{+2} ions; this is indicated by the absence of any diopsidic peak in the X-ray diffraction charts, one of which is presented in *Fig. 6*.

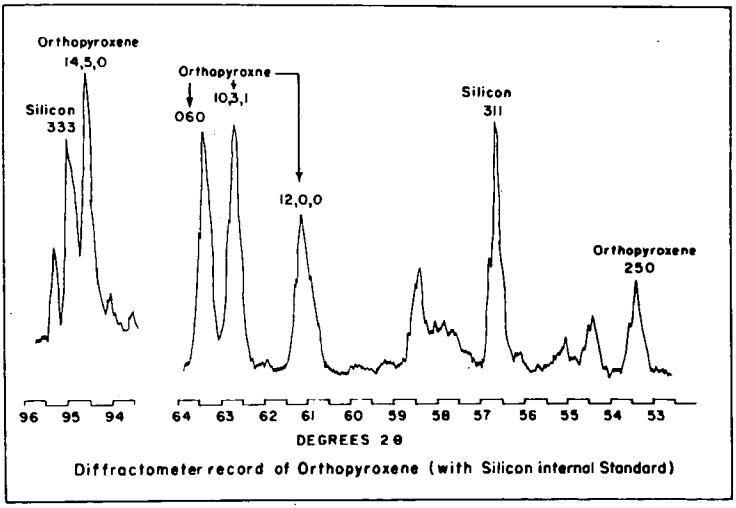

Fig. 6. Diffraction record of orthopyroxene (with silicon internal standard).

The diffraction study of nearly pure orthopyroxenites collected from south of Purnapani village was carried out by Philips high-angle diffractometer. The specimens were finely ground and mixed with pure silicon (as internal standard) and examined as smear mounts. Scans were made from 46°—65° 2Θ, 70°—77° 2Θ and 85°—96° 2Θ. Ni-filtered CuK_α radiation was used with scan speed of 1/8°/min. and chart speed 200 mm. and rate meter $\times 8$. Pulse height discriminator was used to increase peak to background ratios. The 2Θ values were corrected by the use of silicon peaks. Average of three repetitions was used. The 2Θ's (and d-spacings, thus obtained) were accurately measured and were used for the determination of cell parameters using Cohen crystallographic computer programmes for lattice parameter refinement and for calculating expected line position.

In the programme, written in FORTRAN and using Cohen's method (see N. V. COHEN, Rev. Sci. Inst., *6*, [1935] 68, and ibid *7*, [1936], 155), the lines were weighted as 1/2 $\sin^2 2\Theta$ (J. B. HESS, Acta Cryst., *4*, [1951], 209). For refinement of the parameters NELSON—RILEY extrapolation function $\frac{\cos^2\Theta}{\sin\Theta} + \frac{\cos^2\Theta}{\Theta}$ was used, the alternative diffractometer off-axis function ($\cos\Theta \cot\Theta$) was also available. The output from the programme was a list of indexed lines with observed and calculated "*d*" and $\sin^2\Theta$ values for each and the calculated lattice-parameters and their standard deviations; the slope of the extrapolation function and the sum of $(\sin^2\Theta_{calc} - \sin^2\Theta_{obs})^2$ were also printed. The programme rejected lines which were not in agreement with the majority.

An example of the output of the work is shown in Appendix I. The cell parameters shown are:

$a = 8{,}84968 \pm 0{,}00511$ (S.D.) Å
$b = 18{,}20741 \pm 0{,}01140$ (S.D.) Å
$c = 5{,}19721 \pm 0{,}00469$ (S.D.) Å.

Since the indices of reflection were determined from A.S.T.M., which used the space group $D_{2H}^{15} - Pcab$, the *b* and *a* values are interchanged when the space group is taken as Pbcs, as used in the DEER, HOWIE and ZUSSMAN [1963, 2, p. 9].

Some parameters were also manually determined by following RAMBERG and DEVORE [1951]. The a_0 and b_0 cell dimensions were measured initially on 12, 0, 0 and 0, 6, 0 and refined by reference to 14, 5, 0 and 250. The 2Θ positions of these reflections are shown in *Fig. 6*. The c_0 parameter was measured from the weak 004 reflection (73° 2Θ) after HOWIE [1963]. The 2Θ values were corrected by use of the silicon internal standard.

The chemical analyses of the orthopyroxenes (Table 1) have been recalculated to six oxygen atoms and the cations are grouped to *Z* and *WXY* positions (Table 8).

TABLE 8

Ortopyroxene analyses recalculated to 6 oxigens basis

	Serial No.	1	2	3	4	5
	Sample No.	Ex	B124	B123	B68	M434
Z	Si^{+4}	1.9992	1.9231	1.9905	1.9865	1.9803
	Al^{+3}	0.0008	0.0218	0.0095	0.0135	0.0197
W	Al^{+3}	0.0149	—	0.0069	0.0002	0.0052
X	Fe^{+2}	0.0853	0.1636	0.0804	0.0807	0.0968
Y	Mg	1.8681	1.8587	1.8427	1.8537	1.8242
	Ti					
	Ca	0.0346	0.0158	0.0240	0.0183	0.0289
	Na			0.0016	0.0058	0.0016
	K	0.0004	0.0012	0.0012	0.0026	0.0060

According to the general formula of pyroxenes as

$(W)_{1-p}(X, Y)_{1+p}Z_2O_6$

where $W = Ca^{+2}, Na^{+1}$

$X = Mg^{+2}, Fe^{+2}, Mn^{+2}, Ni^{+2}$

$Y = Al^{+3}, Fe^{+3}, Cr^{+3}, Ti^{+4}$

$Z = Si^{+4}, Al^{+4}$.

The orthopyroxene series has $p \simeq 1$ and the amount of trivalent ion in these should be small. The general series Enstatite—Orthoferrosilite has ideally the formula as $(Mg, Fe^{+2})_2 Si_2O_6$.

There is no reason to suggest that other ion than Al^{+3} can enter into the Z position with Si^{+4}. The orthopyroxenes have therefore been divided into two groups WXY and Z and the alumina is distributed between the two in the following manner:

$$Z\,Al^{+3} = X\,Al^{+3} + Z\,Ti^{+4} + Cr^{+3} + Fe^{+3} - Na + K.$$

The recalculated analyses show a systematic substitution of Al^{+3} for Mg^{+2} and Si^{+4}. When calculated in this way the results, given in Table 8, show that there is certain deficiency in the Z group in some samples (B124). There may be solid solution along the orthopyroxene — olivine joint at high pressure [BOYD and ENGLAND 1960]. Similar cation deficiency is observed in the orthopyroxene analyses of peridotite nodules in basalt and alpine-type peridotites quoted by ROSS, FOSTER and MYERS [1954] and in those from Lizard enstatites [GREEN, 1964].

The analyses in general show greater substitution of aluminium for Z silicon than X magnesium.

Electron-probe investigation of bronzite revealed quite high chromium background *(Fig. 3)*. This may be due to distortions in the structure of orthopyroxene. Compounds of Cr^{+2} ions are relatively susceptible to JAHN—TELLER distortions and consequently are relatively enriched in orthopyroxene M_2 sites.

TABLE 9

Alumina in orthopyroxenes from different paragenesis

Paragenesis	Wt.% Al_2O_3	References
Metamorphic (mainly charnockite · granulite)	0.5 —0.95	HOWIE [1963]
Metamorphic (amphibole pyroxene-granulite)	1.25—3.12	SEN and REGE [1966]
Volcanics	0.5 —2.5	DEER, HOWIE and ZUSSMAN [1963, V. 2.]
Stratiform Complexes	0.5 —2.5	DEER, HOWIE and ZUSSMAN [1963, V. 2.]
Alpine-type peridotites	0.7 —6.5	ROSS, FOSTER, MYERS [1954] and GREEN [1964]
Nodules in basalt	2.1 —5.5	ROSS *et al.* [1954]
Garnet peridotite	1—2	O'HARA, MERCY [1963]
Alpine pyroxenit (Sukinda)	0.66—1.20	AUTHOR [1970]

A brief summary of alumina in orthopyroxenes from different parageneses is given in Table 9.

Orthopyroxenes from certain Alpine type peridotites contain relatively large amounts of alumina; in the Lizard orthopyroxenes it varies from 1 to 6,5% [GREEN, 1964]. Sukinda ultrabasics in comparison with other occurrences, mentioned in Table 9, have orthopyroxenes with the lowest range of Al_2O_3 content (0,66—1,20%). The variation of total alumina with the En ratio in Sukinda orthopyroxenes (Tables 1 and 2) is compared with those from various parageneses (*Fig. 7*).

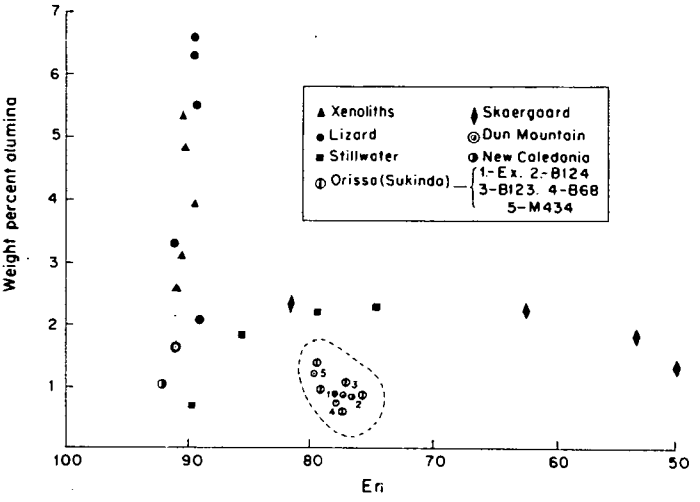

Fig. 7. Relation between weight per cent alumina and molecular per cent En in calcium-poor pyroxenes from plutonic igneous rocks $En = 100\ Mg/Mg + Fe^{2+} + Fe^{3+} + Mn$.

In the Ca-poor pyroxenes of Skaergaard sequence alumina is fairly constant but shows a tendency to decrease at the iron-rich end.

The aluminous orthopyroxenes from the nodules in basalt, Lizard, have very similar En ratios, but show a wide range of alumina content. Total alumina in the orthopyroxenes varies widely and is largely independent of the En ratio, although the greatest amount is found between En_{80} and En_{40}, as can be seen from the analyses quoted by HOWIE [1963]. The majority of these are from charnockites and granulites and it has been suggested that crystallization at high pressure is the condition for the formation of high alumina orthopyroxenes [BOYD and ENGLAND, 1960]. However, not all of them are aluminous. Alumina-rich orthopyroxenes can co-exist with Ca-poor garnet in granulite, free from clinopyroxenes [O'HARA, 1963]: whilst the reverse is true of the majority of the alumina-poor pyroxenes. Orthopyroxenes between En_{80} and En_{40} more readily accommodate alumina than either more magnesium or more iron-rich types [RAMBERG and DEVORE, 1951]. Although this may be partially true of the metamorphic orthopyroxenes the same does not apply for other parageneses.

Pressure may favour the reaction $MgMgSiSiO_6 \rightarrow MgAlAlSiO_6$, because of the resultant decrease in volume [HESS, 1952]. The system $MgSiO_3$—Al_2O_3 has been investigated by BOYD and ENGLAND [1960] who have shown that the maximum alumina substitution in enstatite at 1 bar is 5 p.c., but at 18,000 bars and a temperature of 1400°C up to 14 wt. p.c. alumina, and possibly 19 wt. p.c. can be accommodated in the enstatite structure. However, their experiments were made with synthetic enstatites free from $FeSiO_3$. HOWIE [1963, Table 3, No. B 20] has analyzed a hypersthene from a hornfels containing 7,2 wt.% Al_2O_3 and it is doubtful if this rock formed at high pressure. HESS [1952] suggested that enstatites from peridotite nodules in basalt may have been brought up from the mantle and their high alumina content is a result of pressure or high temperature of crystallization at depth.

On the other hand, garnet peridotites contain low alumina orthopyroxenes and these are considered to have originated at high pressure.

Thermodynamic considerations also suggest that the temperature of crystallization controls the amount of Al_2O_3 entering the pyroxene structure [BUERGER, 1948.]

CALCIUM IN WORLD ORTHOPYROXENES

The lime content of the analyzed Sukinda orthopyroxene varies from 0,43—0,76% and increases slightly with alumina *(Fig. 8)*. Local heterogeneity in the magma of this region, having pockets of higher $P-T$ phases of orthopyroxenes (as partially represented by M 434) is postulated by the author.

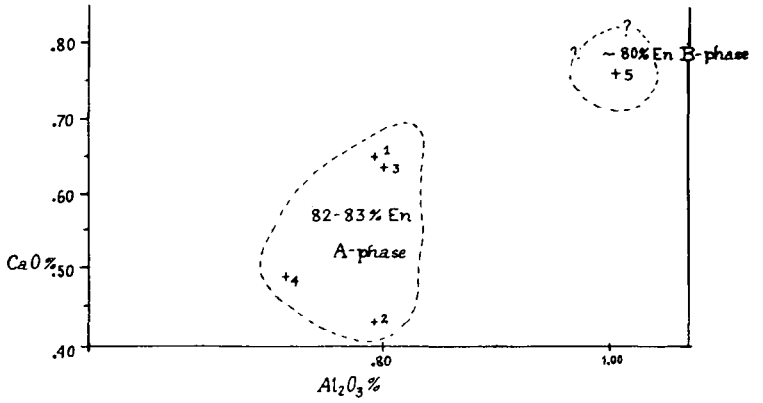

Fig. 8. Plot of CaO% vs. Al_2O_3% in orthopyroxenes. A change in magmatic condition during the crystallization of B-phase (~80% En content) from the possibly earlier A-phase (82—83% En content) formation.

The orthopyroxenes of Sukinda rarely contain fine exsolution lamellae of clinopyroxene, which also supports a peridotite source rather than basaltic. The lamellae, when present, are of the "Stillwater type" as defined by HESS [1960], and are not inverted pigeonites. Orthopyroxenes of Bushveld type have lamellae parallel to 100 [HESS and PHILLIPS, 1938].

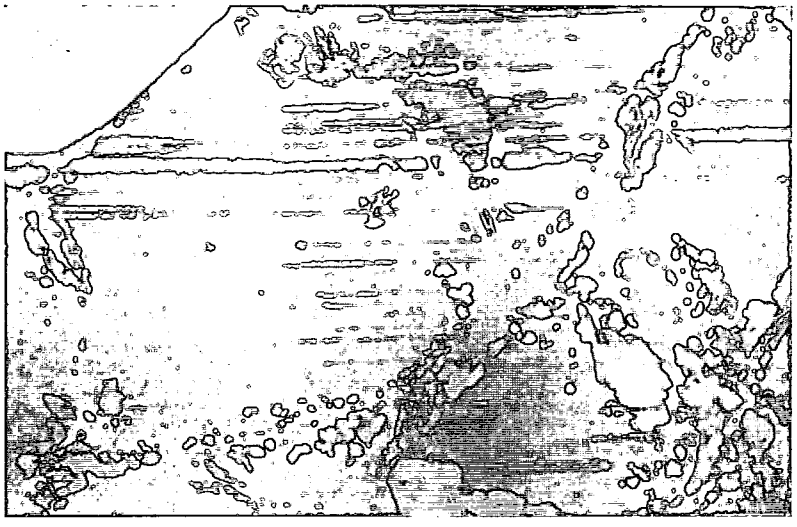

Fig. 9. Twinned orthopyroxene with very fine exsolutions of clinopyroxenes (x 250).

The 100 lamellae are not always attributed to exsolution of clinopyroxenes. The lamellae are due to translation in (100) accompanied by banding about (100). Optical studies of orthopyroxene from the Insizwa intrusion, E. GREENLAND indicated that the lamellar structure is due to multiple twinning about the *Z*-axis [BRUYNZEEL, 1957]. In the Sukinda orthopyroxenes, however, the lamellae, when present, are mostly in optical continuity. Interfaces with common structure are sites of minimal energy requiring unmixing to occur [BUERGER, 1948]. But their optical properties (*e. g.* greater birefringence than that of the host) leave no doubt regarding their exsolution nature. Moreover in serpentinized enstatites the exsolu-

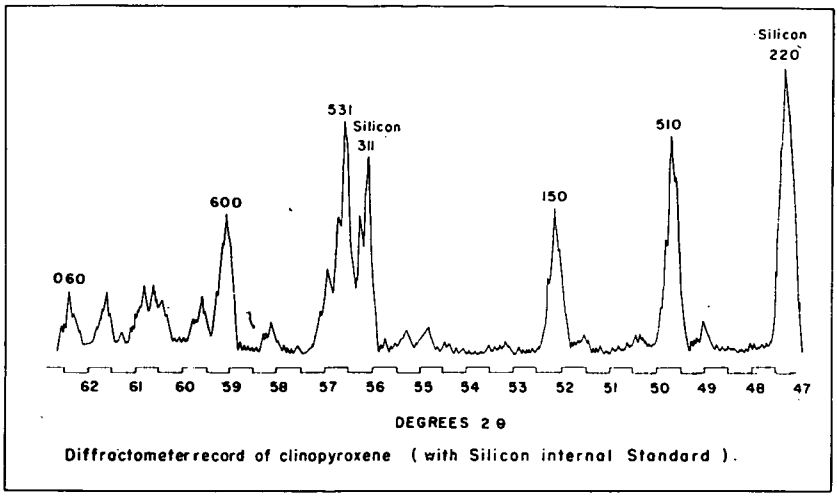

Fig. 10. Diffraction record of clinopyroxene (with silicon internal standard).

tion lamellae are frequently unaltered indicating that they have different compositions than the host *(Fig. 9)*.

Some electron-probe study for Ca and Fe *(Fig. 5)* revealed fine bands of diopside in augitic clinopyroxene co-existing with orthopyroxenes. In places fine (20—30 μ) exsolution of orthopyroxenes in clinopyroxene is also observed *(Fig. 4)*. In most cases background noise due to Cr was quite high. The species of the clinopyroxenes identified are predominantly augite and diopside. These were often determined from the X-ray diffraction chart, a relevant part of the 2Θ range etc. used, is presented in *Fig. 10*.

Orthopyroxenes of Bushveld type crystallized below the inversion temperature of orthorhombic to monoclinic pyroxenes (approx. 1140 °C) and the exsolution was due to slow cooling; whereas the poorly developed lamellae in orthopyroxenes in Sukinda suggest that these were formed by faster cooling of the crystallizing peridotite magma.

The coef. of correlation (γ) between Al_2O_3 and CaO is 0,7509 and the regression equation for these is

$$Al_2O_3 = 0{,}1458 + 0{,}011721\ CaO.$$

CONCLUSION

The occurrence of dunite and pyroxene-bearing peridotite viz., harzburgite websterite, wehrlite and lherzolite in the present area suggests that crystallization of these took place from differential layers of their own bulk composition in an Al_2O_3-free ultrabasic magma.

The implication of lime content in the enstatites of Sukinda lies in shifting the pointer towards an ultramafic (peridotite) magma indicating it as the parent magma in the present area of the Eastern Ghat region of Eastern India. Search of literature has not brought out any experimental evidence that liquids close to orthopyroxenite in composition can be produced by partial fusion of peridotites in any pressure-temperature environment. It is therefore concluded that the rocks that fused to produce the Sukinda magma were compositionally unlike any present day upper mantle magma genetic zones. The intrusive magma, however, could be contaminated with the primitive rocks, which might have changed the path of crystallization.

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ENSTATITE

PROGRAM COHEN CASE 12/1967/01
TWO THETA CORRECTION 0.000
REJECTED LINES. ERROR = 0.00400
NONE
REJECTED LINES. ERROR = 0.00360
NONE
REJECTED LINES. ERROR = 0.00320
NONE
REJECTED LINES. ERROR = 0.00280
NONE
REJECTED LINES. ERROR = 0.00240
NONE
REJECTED LINES. ERROR = 0.00200
NONE
REJECTED LINES. ERROR = 0.00160
NONE
REJECTED LINES. ERROR = 0.00120
NONE
REJECTED LINES. ERROR = 0.00080
NONE
LINE USED

Space Group S. G. D_{2h}^{15} – PcAB

H	K	L	D OBS	D CALC	DELATA D	SIN SQ THETA OBS	CALC	DIFF
1	2	0	6.35271	6.34361	0.00910	0.01985	0.01991	—0.00006
2	0	0	4.41401	4.42390	—0.00990	0.04112	0.04094	0.00018
2	1	1	3.30579	3.31240	—0.00661	0.07332	0.07302	0.00029
2	4	0	3.17029	3.17233	—0.00203	0.07972	0.07961	0.00010
2	2	1	3.17029	3.15925	0.01104	0.07972	0.08027	—0.00056
2	3	1	2.94410	2.94531	—0.00121	0.09244	0.09236	0.00008
1	6	0	2.87348	2.87013	0.00335	0.09704	0.09726	—0.00023
1	5	1	2.82834	2.82577	0.00257	0.10016	0.10034	—0.00018
2	4	1	2.70822	2.70772	0.00050	0.10924	0.10928	—0.00004
3	1	1	2.53816	2.54008	—0.00191	0'12437	0.12418	0.00019
0	2	2	2.49773	2.49853	—0.00080	0.12843	0.12835	0.00008
3	4	0	2.47412	2.47524	—0.00112	0.13089	0.13077	0.00012
2	5	1	2.47412	2.47276	0.00136	0.13089	0.13103	—0.00014
3	6	1	1.95823	1.95900	—0.00077	0.20894	0.20878	0.00016
2	9	1	1.73291	1.73428	—0.00138	0.26681	0.26638	0.00043
5	5	1	1.52284	1.52199	0.00085	0.34549	0.34588	—0.00039

PROGRAM COHEN CASE 12196701
NELSON—REILEY EXTRAPOLATION
DIFFRACTOMETER COS THETA X COT THETA EXTRAPOLATION
WEIGHTING FUNCTION COSEC SQUARED TWO THETA

PARAMETER S. DEV

A = 8.84968 ± 0.00511 Å
B = 18.20741 ± 0.01140 Å
C = 5.19721 ± 0.00469 Å

QEW = 9.68E-07
SLOPE = 8.91E-05 3.94E-04

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MANIFESTATIONS OF THE CHANGES OF UPPERMOST TERTIARY AND QUATERNARY SOURCE AREAS IN THE JÁSZSÁG BASIN

B. MOLNÁR and Á. FEKETE

INTRODUCTION

In the course of the mapping of the Great Hungarian Plain the Hungarian Geological Survey has aimed both at exploring the geology of the land surface and studying the deeper-seated subsurface aquifers. Therefore several cored boreholes were sunk to considerable depths so as to reach down to both the Pleistocene and much of the Pliocene (Pannonian and Levantine) sequence. The geological processing of the cores recovered from these boreholes has allowed the author to examine, beside exploring the water-bearing strata, the mineralogical and petrographical composition of the Great Hungarian Plain's uppermost Pliocene and Quaternary formations and to give a more correct interpretation of the geohistorical evolution of the area as deduceable from the results.

In the Great Hungarian Plain's Jászság Basin at Jászladány a core-drilling of 950 m depth was undertaken *(Fig. 1)*. Under the direction of A. RÓNAI [1966, 1969a, 1969b, 1972] the paleontological and lithological elaboration of the lithological logs of the drilling had been performed already earlier. During that work A. RÓNAI showed the lowermost reaches of the log, 735 to 950 m, to be composed of Upper Pannonian shallow-water lacustrine to palustrial sediments, the 430 to 735 m interval to consist of Upper Pliocene (Levantine) terrestrial sediments, and the uppermost 430 m to be constituted by predominantly unconsolidated detrital Pleistocene sequences. A. RÓNAI also showed that the Pleistocene sedimentary sequence is of cyclical structure due to crustal movements. According to B. MOLNÁR [1972], the cycles here are symmetrical and both the Pleistocene and the Pliocene intervals are characterized by a cyclicity.

During the lithological processing of the profile of the borehole I. MIHÁLYI—LÁNYI [in RÓNAI, A. 1968, 1972] determined the micromineralogical composition of the sand samples recovered. She deduced, however, her conclusions from the determinations of merely a hundred grains. It is well-known that in sand sample containing a great number of mineral variants one hundred grains are insufficient for obtaining the correct result [DRYDEN, A. L. 1931; MOLNÁR, B. 1959, 1970]. I. MIHÁLYI—LÁNYI, in evaluating the results, did not take into consideration the remarkable dependence of the heavy mineral composition on the variation of sand grain size either. As for the percentage distribution of quartz, plagioclase and potash feldspar, their characteristic and ratios, she did not even study them.

With a view to its great significance and to its other detailed geological processing, it would be desirable to re-examine the core material in order to meet the

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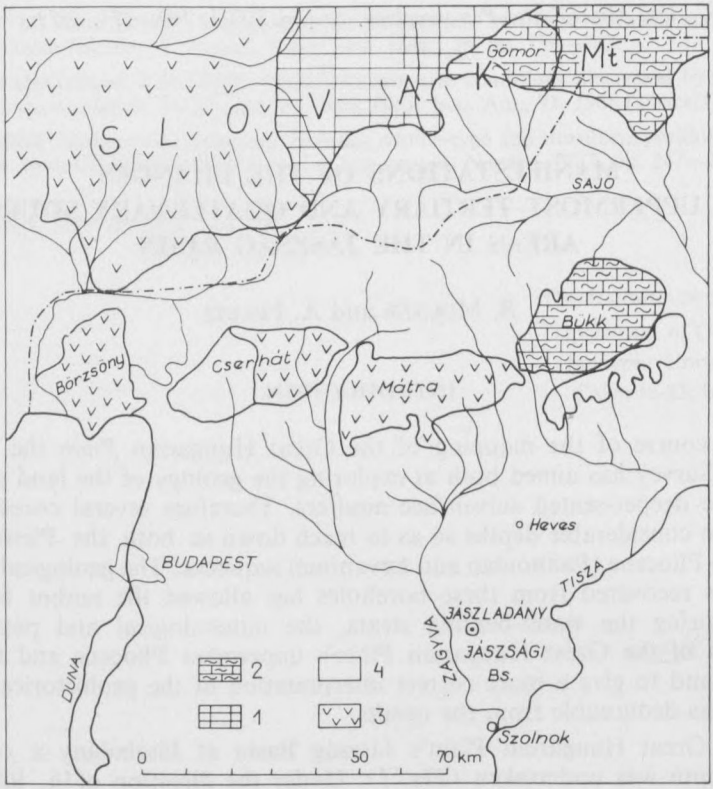

Fig. 1. Lithology of the Jászság Basin and of the areas to the north of it *1.* Crystalline schist *2.* Carbonate rocks, *3.* Volcanic rocks, *4.* Detrital rocks

afore-mentioned requirements. Namely, the results that may thus be obtained can be used as a basis for comparison with further drilling data and they may help assess more correctly the latest Pliocene and Pleistocene history of the area as well.

EXAMINATION OF THE MINERALOGICAL COMPOSITION OF SAND SAMPLES FROM THE JÁSZLADÁNY BORE PROFILE

Selecting of the samples and their preparation for analysis

As far as it was possible, sands of subidentical to identical predominant granulometric composition were selected for analysis (Table 1). Thus the author also attempted to avoid possible errors due to grain size differences. *Nota bene*, as shown by earlier comparative studies, it is favourable to select small-grained sands (0,1—0,2 mm) for analyzing the heavy mineral composition of the Great Hungarian Plain's Pliocene and Pleistocene sands [B. MOLNÁR, 1970].

It is in the case of this granulometric composition that the results can be correlated with one another. The investigations have also shown that the 0,1 to 0,2 mm fraction of small sands is advantageous to analyze. In the Great Plain's Pliocene

and Pleistocene sediments in this fraction the striking concentration of garnet and magnetite towards the finer grain sizes cannot yet be observed, but mica and chlorite also fail to increase in concentration towards the coarser fractions. Instead, the sample yields the most favourable heavy mineral composition.

Therefore the author has selected for further research the small sand fraction or — where only fine sand was available in the studied interval — the 0,1 to 0,2 mm fraction of fine sands in the Jászladány profile as well. This fraction was separated conventionally (with bromoform) into a portion of light and a portion of heavy specific weight.

Using mineralogical microscope, the author determined 250 to 300 grains from the heavy mineral fraction of each sample and he calculated then therefrom the percentage quantities of the individual minerals within the sample. Namely, according to A. L. DRYDEN [1931], the possible error will markedly decrease at about 300 grains determined. The Great Hungarian Plain's Pliocene and Pleistocene sediments contain, as a rule, 15 to 25 different heavy minerals. If in these sediments the minerals are present in the afore-mentioned number and if one wishes to determine only the predominant minerals sufficient for locating the catchment area of the transporting river, it is enough to determine 200 or eventually 150 grains. If, however, the determination of the quantity of minerals present in low amount is also attempted, at least 300 grains or more have to be determined [B. MOLNÁR, 1970]. Accordingly, the figure of 250 to 300 grains determined can be said to be the optimum for the present purpose.

The obtained results have been grouped — as far as it was possible — according to the origin of the minerals (Table 1).

After separation on bromoform the residual light fraction was used for the determination of the quantity of quartz, plagioclase and potash feldspar as wel as for the examination of the forms of occurrence of the light minerals. In quantitative analyses the colouring process developed by BAILEY and STEVENS [1960] was applied.

The Jászladány sand samples are loose, unconsolidated, therefore the sand grains before analysis were first mounted in Canada balsam on the object plate and they were then pressed down softly to the object plate. Afterwards the slide was polished with the finest abrasive powder so as to possibly half the 0,1 to 0,2 mm grains. This way a smooth surface corresponding in size to most of the grains was obtained.

After painting 1000 grains per sample were determined under binocular stereomicroscope for the determination of the most appropriate proportion of minerals within the fraction. According to E. D. JACKSON and D. D. ROSS [1956] namely, this number of grains is already sufficient for the determination of the proper mineral ratio.

Evaluation of the heavy mineral analyses

Evaluating the data summarized in Table 1, let us conclude that in the Jászladány drilling profile, between the surface and the deepest sand sample recovered from 915 m depth, five major changes in source area can be recognized. Let us quote them:

1. The heavy mineral composition of the *Upper Pannonian* is characterized by the relatively small number of minerals. The column diagram of the calculated weighted averages of the most essential minerals of the seven samples encompassing the Upper Pannonian interval indicates that the sequence under consideration contains but a few minerals, of which chlorite is present in a striking quantity. (Minerals having values below 1% have not been represented for technical reasons, see *Fig. 2.*)

In the sequence, characteristic minerals beside chlorite are garnet, other representatives of pyroxene (predominantly bronzite), magnetite-ilmenite, limonite and weathered minerals. The minerals diagnostic for the Upper Pannonian interval and distinguishing it from the overlying sequence have been distinguished by framing the respective items in Table 1. That the formation has a simple mineralogical composition is proved by the diagram of *Fig. 3*, too, in which predominantly chlorite, a few weathered minerals and one apatite grain can be observed.

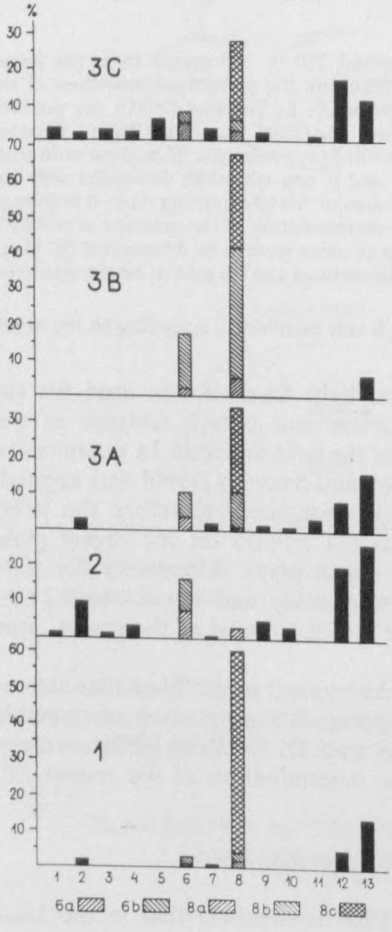

Fig. 2. Averages of minerals predominant in horizons of different heavy mineral composition of the Jászladány drilling profile

1. Upper Pannonian, *2.* Upper Pliocene (Levantine) — Pleistocene *3A*, *B*, *C* horizons *1.* Hypersthene, *2.* Other rhombic pyroxenes, *3.* Augite, *4.* Diopside, *5.* Basaltic hornblende, *6.* Magnetite-ilmenite *(6a)* and limonite *(6b)*, *7.* Apatite, *8.* Biotite *(8a)*, chloritized biotite *(8b)* and chlorite *(8c)*, *9.* Tourmaline, *10.* Rutile, *11.* Hornblende, *12.* Garnet, *13.* Weathered minerals

Accordingly, on the basis of the heavy mineral composition, the material of the Upper Pannonian formation derives from a slightly metamorphosed source area or it has originated from the redeposition of chlorite-rich sediments.

2. From the *Upper Pliocene (Levantine)* formation, 13 samples have been analyzed for heavy mineral composition. A substantial change with regard to the Upper Pannonian formation can be observed. In the Levantine formation there appear a greater number of minerals as compared to those observed in the Pannonian. This is warranted by the diagram of *Fig. 2* showing essentially more mineral variants.

Mineral comoposititon of the Upper Pannonian, Upper Pliocene (Levantine) and Pleistocene sands of the Jászladány borehole

TABLE 1.

Number	Depth m	HEAVY MINERALS: Dominantly magmatic minerals: Hypersthene	Other rhombic pyroxenes	Augite	Diopside	Basaltic-Hornblende	Magnetite—Ilmenite	Apatite	Zircon	Biotite	Chloritized Biotite	Dominantly metamorphic minerals: Chlorite	Tourmaline	Epidote	Zoizite	Rutile	Hornblende	Actinolite—Tremolite	Garnet	Staurolite	Kyanite	Glaukophane	Other minerals: Calcite-dolomite	Clastic carbonate	Limonite	Pyrite	Other micas	Weathered minerale	Total quantity minerals in the examined fraction	Light minerals: Quartz	Plagioklase	K-felspar	Quartz—felspar ratio	Plagioklase—K-felspar ratio	Dominant grain diameter mm	Age
1	32,50— 32,68	5,2	0,7	4,1	0,4	4,5	3,4	3,4	—	1,9	7,9	23,2	2,2	1,5	—	0,7	6,4	1,1	4,9	—	—	—	3,4	—	3,4	3,4	2,2	16,1	1,6	61	28	11	1,56	2,54	0,06—0,1	C
2	33,22— 33,51	7,5	2,6	4,5	2,6	2,2	3,7	2,6	0,7	1,1	6,3	15,7	0,7	2,2	0,4	0,7	3,0	1,5	23,5	0,7	0,7	—	1,1	—	2,2	2,6	1,5	9,7	3,2	42	38	20	0,72	1,90	0,06—0,1	
3	44,87— 45,26	1,6	—	1,6	1,0	5,2	2,0	1,0	—	7,8	1,0	47,8	2,0	1,0	—	1,6	0,5	—	10,1	—	0,5	—	1,6	—	1,0	—	0,5	10,4	1,8	65	25	10	1,85	2,50	0,06—0,1	
4	57,71— 58,50	0,9	2,8	3,8	1,4	12,7	2,8	3,8	0,5	3,3	0,5	21,3	3,8	1,4	0,5	0,5	1,9	0,9	15,1	—	1,4	—	2,8	—	5,2	2,8	0,9	9,0	0,6	75	17	8	3,00	2,12	0,06—0,1	
5	60,25— 60,63	0,4	1,6	3,7	2,6	7,0	5,3	2,9	—	2,5	1,6	20,6	2,5	0,8	0,4	0,8	1,6	—	20,2	—	1,2	—	1,2	—	3,3	2,9	2,5	14,4	0,8	63	26	11	1,70	2,36	0,06—0,1	
6	81,65— 82,10	2,9	2,9	0,4	5,3	2,0	7,8	3,7	—	0,8	1,2	11,5	2,0	1,2	—	0,8	2,9	—	30,2	0,4	0,4	0,4	0,8	5,3	2,0	2,0	0,4	12,7	1,2	69	21	10	2,22	2,10	0,06—0,1	
7	97,17— 97,51	1,9	2,2	1,1	0,8	6,3	6,7	3,4	—	1,1	5,6	28,0	2,6	2,6	1,5	1,5	1,9	—	11,2	—	—	—	1,9	2,6	4,1	2,6	1,1	9,3	0,5	63	23	14	1,70	1,64	0,1 —0,2	
8	122,62—122,70	3,3	3,3	2,6	3,7	5,9	10,3	7,0	—	2,6	—	10,0	3,3	1,8	1,8	0,7	1,1	0,7	19,4	—	1,1	—	2,6	0,7	1,5	5,6	0,7	10,3	0,5	69	18	13	2,22	1,38	0,06—0,1	
9	130,87—131,40	0,6	—	—	0,6	—	—	0,6	—	8,1	32,6	30,3	—	1,1	—	0,6	—	—	0,6	—	—	—	0,6	—	18,3	—	1,1	4,9	1,6	47	33	20	0,88	1,65	0,06—0,1	
10	165,50—166,50	—	0,5	—	—	1,5	8,1	2,5	—	1,0	14,1	28,9	1,0	0,5	0,5	0,5	2,5	—	2,0	—	—	—	—	—	19,7	0,5	3,6	12,6	1,0	63	24	13	2,62	1,84	0,1 —0,2	
11	167,26—168,06	0,9	—	0,5	—	—	1,7	—	—	1,7	10,7	27,9	—	—	—	—	0,5	—	0,9	—	—	—	0,5	—	39,8	—	0,5	14,4	0,4	56	28	16	1,27	1,75	0,06—0,1	B
12	178,73—178,83	—	—	—	—	—	—	1,3	—	8,6	63,6	25,8	—	—	—	—	0,7	—	—	—	—	—	0,7	—	—	—	7,3	2,0	2,1	45	32	23	0,81	1,39	0,06—0,1	
13	179,16—179,25	—	—	—	—	—	—	—	—	5,2	71,6	16,5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4,5	2,2	2,4	49	31	20	0,96	1,55	0,06—0,1	
14	191,20—191,57	0,7	1,5	1,6	1,1	1,1	3,3	4,1	—	2,2	15,9	19,1	1,1	—	1,1	0,7	1,6	—	6,7	—	0,7	0,7	—	—	8,9	0,7	4,8	21,6	0,1	56	18	26	1,27	0,69	0,06—0,1	
15	202,18—303,40	0,7	3,3	1,5	1,8	0,4	11,0	1,8	—	0,7	5,1	13,6	2,9	0,7	0,7	0,7	1,1	—	11,0	—	—	0,7	—	—	16,5	0,4	2,2	23,5	0,4	63	19	18	1,70	1,05	0,06—0,1	
16	245,00—245,50	—	—	—	0,8	—	—	—	—	—	60,3	19,8	—	0,8	—	—	1,6	—	2,4	—	0,8	—	—	0,8	—	—	2,4	10,3	0,5	57	25	18	1,32	1,38	0,06—0,1	
17	272,50—273,06	1,0	2,0	1,0	0,7	2,4	9,9	1,5	—	—	25,6	15,3	2,0	0,7	0,4	0,7	2,7	1,0	8,2	—	—	0,4	—	—	6,1	—	4,8	13,6	0,9	59	20	21	1,43	0,95	0,1 —0,2	
18	287,82—287,98	1,6	3,3	0,3	0,7	1,3	5,2	6,5	—	1,0	1,3	17,6	3,3	2,6	—	2,9	9,4	0t7	15,5	—	0,3	0,7	0,3	—	5,9	—	1,3	18,3	0,3	54	36	10	1,17	3,60	0,1	
19	290,82—291,16	1,0	2,9	0,7	2,6	1,3	8,5	2,0	—	0,3	6,2	15,0	4,2	1,0	0,3	1,0	4,2	0,3	17,6	—	0,3	1,0	—	—	5,2	0,3	5,6	18,5	0,2	70	19	11	2,33	1,72	0,1	
20	299,58—299,69	0,4	0,9	1,3	0,9	—	5,8	2,7	0,4	1,8	30,1	11,5	0,4	0,4	0,9	0,9	0,4	—	6,6	—	—	—	0,4	—	11,0	—	3,1	18,1	0,3	59	19	22	1,43	0,86	0,1	
21	317,00—317,31	0,7	0,7	0,7	—	—	8,8	1,6	—	0,3	11,4	17,7	1,6	—	0,3	0,3	0,3	0,3	10,7	—	—	—	—	—	20,8	—	3,6	20,2	0,6	67	8	25	2,03	0,53	0,1	
22	324,50—325,10	0,7	1,8	0,4	0,7	0,7	5,6	2,1	1,1	1,4	7,7	31,3	5,6	0,4	—	4,6	2,1	0,4	11,2	—	—	1,1	0,4	—	7,0	—	4,2	9,5	0,2	55	37	8	1,22	4,62	0,1	A
23	332,32—333,16	—	4,4	0,4	3,0	—	—	2,2	—	6,3	5,2	36,5	0,7	0,7	1,1	0,4	7,0	4,4	4,1	—	1,5	—	1,8	—	1,1	—	6,3	12,9	1,3	45	34	21	0,81	1,61	0,1	
24	353,47—353,80	1,6	6,3	1,6	2,3	0,4	2,7	3,1	—	—	—	5,1	2,0	0,4	0,4	3,9	3,1	0,4	21,7	—	—	1,2	—	—	16,4	—	2,0	25,4	0,4	73	17	10	2,70	1,70	0,1	
25	365,14—365,31	—	—	—	—	0,5	—	—	—	2,3	8,8	48,4	—	0,5	—	1,8	2,8	1,8	—	—	—	—	—	—	1,8	9,2	3,2	18,9	1,3	47	46	7	0,88	6,57	0,06	
26	389,02—389,37	0,6	—	—	—	7,2	—	0,6	—	—	—	5,0	1,7	—	0,6	1,1	1,1	0,6	3,9	—	—	—	—	55,0	7,0	—	—	15,6	0,9	74	15	11	2,96	1,36	0,1 —0,2	
27	395,14—395,96	0,7	5,5	1,1	2,9	—	—	1,5	0,4	0,4	1,1	29,0	0,4	0,4	0,4	—	9,6	1,8	6,6	—	2,6	—	4,0	3,7	2,2	9,6	4,0	12,1	0,8	53	17	30	1,12	0,56	0,1	
28	410,50—414,17	0,7	17,0	2,1	9,0	—	—	1,7	0,7	—	—	12,5	1,0	3,1	1,0	0,3	2,4	0,7	12,8	0,7	2,1	—	0,7	—	6,9	2,1	4,2	18,0	0,7	39	32	29	0,64	1,10	0,1	
29	417,74—418,48	0,8	1,7	—	1,3	0,8	0,8	0,8	—	0,4	0,8	41,8	—	0,4	0,4	—	1,3	—	1,3	0,4	0,8	—	18,5	5,5	0,8	7,4	5,0	8,0	3,1	52	24	24	1,08	1,00	0,1	
30	428,00—428,86	—	2,4	—	2,6	0,9	0,9	2,0	—	—	0,9	40,1	1,6	1,6	1,2	1,2	1,6	0,9	2,4	—	0,9	—	5,3	0,9	1,2	8,9	13,0	10,1	0,3	47	36	17	1,30	2,11	0,06—0,1	
31	438,50—438,60	2,0	5,6	1,2	1,2	—	5,2	—	—	—	1,2	4,4	5,2	0,4	0,4	1,6	0,4	—	9,6	0,8	0,4	0,8	1,2	2,8	44,4	2,4	1,6	7,2	0,2	62	26	12	1,63	2,16	0,1	2 Upper Pliocene (Levantine)
32	443,81—444,21	0,7	5,2	2,6	1,9	0,4	2,6	0,7	—	0,4	—	4,1	7,4	0,4	0,4	5,9	—	—	15,2	0,4	—	1,5	0,7	—	14,5	2,6	1,1	31,3	0,3	75	14	11	3,00	1,27	0,06—0,1	
33	449,42—450,42	0,7	5,9	0,7	3,1	—	8,0	1,4	—	—	—	2,4	8,3	—	—	5,9	0,4	—	17,3	0,4	0,4	0,7	—	—	11,0	—	1,4	32,0	0,5	74	15	11	2,96	1,36	0,1 —0,2	
34	491,65—492,45	1,0	4,6	1,3	2,6	—	3,3	1,0	0,3	—	0,7	1,0	7,6	0,7	1,3	5,6	—	—	19,5	—	0,7	—	—	—	10,3	—	2,6	35,9	0,1	75	16	9	3,00	1,77	0,1	
35	567,50—567,70	1,7	7,0	—	2,2	0,4	0,4	—	—	—	—	1,7	6,5	0,9	—	8,7	—	—	14,3	—	—	—	—	—	6,5	—	1,3	48,8	0,2	57	33	10	1,32	3,30	0,1	
36	613,35—614,70	1,7	10,1	5,0	3,4	—	14,0	2,1	—	—	—	—	3,4	1,7	0,4	2,1	—	—	31,2	—	0,8	—	—	—	4,2	—	—	19,9	1,4	56	26	18	1,27	1,44	0,1	
37	616,00—617,50	0,8	10,0	5,0	2,5	—	10,2	2,5	0,4	0,4	—	3,3	5,0	2,1	0,8	1,7	—	—	25,5	1,3	2,5	—	0,4	—	4,6	—	—	21,0	2,2	68	23	9	2,12	2,55	0,2 —0,5	
38	664,97—665,37	0,8	17,2	4,3	5,5	—	6,3	1,2	1,2	—	—	4,7	5,5	4,7	0,4	1,6	—	0,4	16,0	2,0	0,8	—	—	—	2,4	—	—	26,0	0,6	63	20	13	1,90	1,53	0,06—0,1	
39	670,70—671,63	1,6	15,1	1,2	3,7	—	12,0	3,7	0,5	—	—	5,3	2,9	2,5	—	2,0	—	—	25,0	0,5	2,5	—	—	—	—	—	0,5	21,0	2,0	69	24	7	2,22	3,42	0,1 —0,2	
40	678,66—679,01	1,9	16,3	3,1	9,0	—	15,1	4,7	0,4	—	—	3,1	1,9	—	0,4	1,6	—	—	17,4	—	1,2	—	—	—	—	—	1,2	22,7	0,9	69	26	9	1,97	2,88	0,06—0,1	
41	715,40—718,70	2,8	9,8	1,2	4,5	—	8,5	2,8	0,8	—	0,4	3,3	2,4	2,0	—	1,2	2,8	—	32,1	0,4	1,2	—	—	—	1,2	—	1,2	21,4	1,1	61	29	10	1,56	2,90	0,1 —0,2	
42	740,40—741,40	1,9	5,2	2,2	1,9	—	5,6	2,2	0,4	—	0,4	25,0	2,6	1,5	—	1,5	5,6	1,1	19,6	0,4	—	—	0,4	—	—	0,7	1,5	20,1	5,0	58	28	14	1,38	2,00	0,06—0,1	1 Upper Pannonian
43	750,60—750,88	—	0,7	—	0,7	—	—	0,7	—	—	—	66,9	0,7	—	—	—	—	—	0,7	—	—	—	2,9	—	14,0	—	—	12,7	0,9	57	31	12	1,32	2,58	0,06	
44	759,75—759,95	—	3,1	0,5	0,5	—	—	—	—	1,0	—	45,8	1,0	—	—	—	2,1	0,5	4,7	—	0,5	—	3,6	—	—	18,8	2,7	15,3	1,7	52	32	16	1,36	2,00	0,1 —0,2	
45	773,30—773,95	—	1,4	—	—	—	0,7	—	—	2,0	8,8	64,6	—	—	—	—	0,7	—	1,4	—	—	—	0,7	—	—	0,7	6,8	12,2	2,1	46	29	25	0,71	1,16	0,06—0,1	
46	777,00—778,00	—	1,9	—	0,9	—	—	—	—	2,8	—	83,3	0,9	—	—	—	2,8	—	0,9	—	0,9	—	—	—	—	0,9	0,9	2,8	2,4	70	8	22	2,33	0,36	0,1 —0,2	
47	889,56—889,75	0,8	1,8	—	1,8	—	2,7	4,9	—	1,3	4,0	35,4	1,3	0,4	0,4	0,4	—	—	5,3	—	—	—	11,1	—	—	4,0	1,8	22,6	0,3	40	41	19	0,66	2,15	0,06	
48	915,12—915,55	—	0,8	—	—	—	—	0,8	—	5,0	3,3	72,5	—	0,8	—	—	—	—	0,8	—	2,5	—	—	—	—	—	—	13,5	0,5	51	37	12	1,04	3,08	0,06	

Outnumbering the 6 minerals or mineral groups of the Pannonian, the mineral groups occurring in the Levantine are already 11 in number. One of the most remarkable changes of the Levantine formation with regard to the Upper Pannonian consists just in the fact that chlorite decreases greatly, being reduced to just a few per cent in contrast with the figure of about 60% in the former case.

Considerable role is played in the Levantine formation by the other rhombic pyroxenes (predominantly bronzite) and magnetite-ilmenite and limonite. The appearance of these minerals in the formation indicates that the source must have included a magmatic area. The presence of a volcanic mountain (Mátra) in the marginal zone was a guarantee for such a magmatic supply still in Levantine time *(Fig. 1)*.

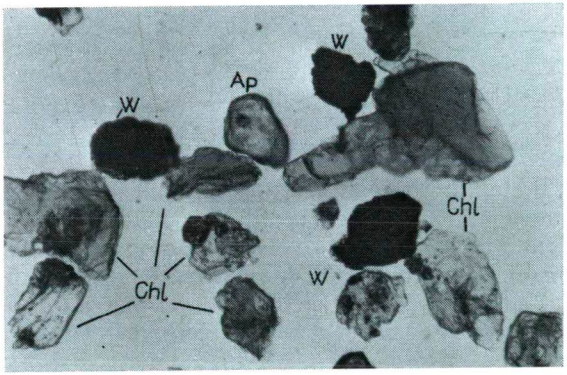

Fig. 3. Heavy minerals of Upper Pannonian sands from 889,5 to 889,7 m of the Jászladány drilling profile H: Hypersthene, OP: Other ortho-rhombic pyroxenes, BH: Basaltic hornblende, AP: Apatite, ChB: Chloritized biotite, Chl: Chlorite, T: Tourmaline, A—T: Actinolite-tremolite, Ho: Hornblende G: Garnet, Ky: Kyanite, Clc: Clastic carbonate, W: Weathered minerals. The photographs were made under mineralogical microscope in plane-polarized light with the minerals mounted in Canada balsam. Magnification: 80 to 100 x.

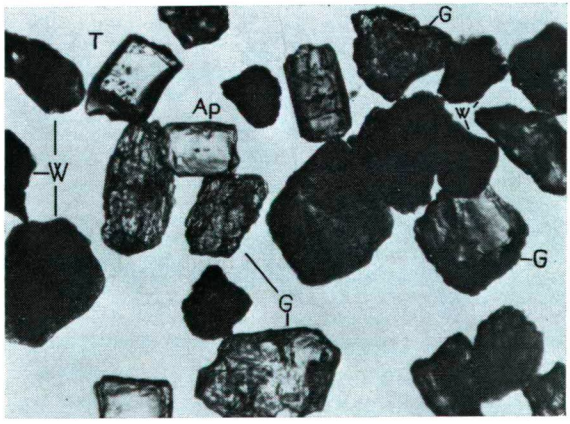

Fig. 4. Heavy minerals of the Upper Pliocene (Levantine) sands deriving from the 613,35 to 614,70 m interval of the Jászladány drilling (For explanation, see *Fig.3*)

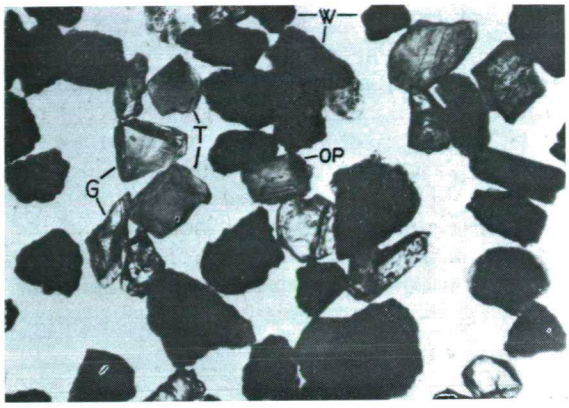

Fig. 5. Heavy minerals of the Upper Pliocene (Levantine) sands deriving from the 443,8 to 442,2 m interval of the Jászladány drilling (For explanation, see *Fig. 3*)

Interesting is the relatively high quantity of rutile which may indicate, unlike the previous magmatic minerals (suggestive of a magmatic source area), the influence of the Slovak Metalliferous Mountains constituted by metamorphic schists and containing some rutile; eventually, the pegmatitic supply of the Mátra Mts. of volcanic origin may also have contributed to the accumulation of rutile. It is here that the quantity of the weathered minerals is the highest in the entire drilling log.

Examples for the heavy mineral composition of the Levantine formation are shown by *Fig. 4.* and *Fig. 5.* It is striking in both, that, in contrast with the monotonous Upper Pannonian, predominantly chloritic, of *Fig. 3*, the representatives of chlorite almost completely lack here. In *Fig. 4*, tourmaline, apatite, garnet and weathered minerals appear. *Fig. 5* shows minerals similar to the former as well as other representatives of pyroxene.

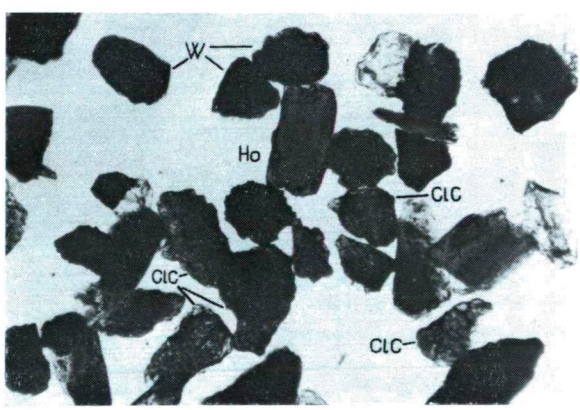

Fig. 6. Heavy minerals of the Pleistocene sands of Horizon *3A* from the 417,7 to 418,1 m interval of the Jászladány drilling (For explanation, see *Fig. 3*).

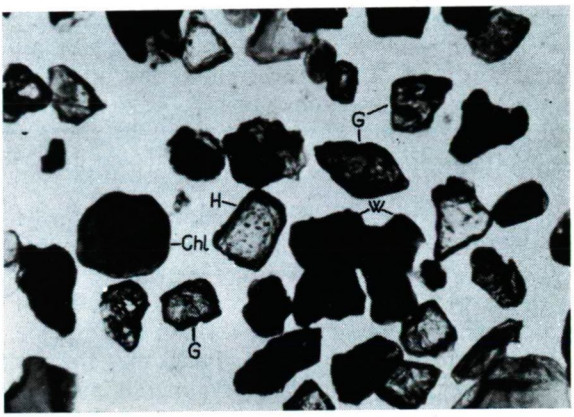

Fig. 7. Heavy minerals of the Pleistocene sands of Horizon *3A* from the 324,5 to 325,1 m interval of the Jászladány drilling (For explanation, see *Fig. 3*)

On the basis of the above let us conclude that the Levantine formation differs from the Upper Pannonian one and that its source area must have included both a metamorphic zone (with a possible redeposition of chlorite-rich sediments) and a magmatic one.

3. The greatest number of analyzed samples, about 30, have been recovered from the *Pleistocene* formation. The composition of the Pleistocene formation shows a substantial change as compared to the Levantine. The Upper Pannonian and the Levantine formations cannot be further subdivided on the basis of their heavy mineral composition. Within the Pleistocene formation, however, three horizons of different heavy mineral composition can be distinguished. In Table 1 and *Fig. 2*, these are indicated as *3 A*, *B*, *C*.

3 A. Within the Pleistocene formation the first heavy mineral horizon can be found in the 191 to 428 m interval. The heavy minerals of this horizon differ from those of the Levantine formation by the lower quantity of magmatic and weathered minerals and garnet in it *(Fig. 2)*. The percentages of common hornblende and chlorite, however, are somewhat higher.

Remarkably enough, the quantity of carbonates, particularly so of detrital carbonate, shows a considerable increase in the lower part of the horizon *(Fig. 6)*

Out of the 13 minerals represented in *Fig. 2*, nine occur in a quantity higher than 1%. Accordingly, the number of such minerals is only a little lower than in the previous horizon. Therefore this horizon too can be said to be rather diversified, as evidenced by the diagram of the sand sample recovered from this horizon, in which chlorite, garnet and weathered minerals are represented *(Fig. 7)*.

On the basis of the heavy mineral composition the material of the horizon derives from sources of mixed genesis.

3 B. The second horizon within the Pleistocene formation, 130 to 179 m interval, shows a composition much simpler than the former. In *Fig. 2* only three mineral groups figure in this horizon. With this low number of minerals the horizon of poorest heavy mineral content of the entire drilling log can be identified. Of the three mineral groups, striking is the quantity, nearly 70%, of biotite, chloritized biotite and chlorite.

The high percentage of chloritized biotite is conspicuous. It is a matter of common knowledge, that in igneous rocks the biotite can be altered into chlorite as a result of autohydration or of hydrothermal action and also in the course of weathering. The chloritized biotites occurring here seem to derive from this kind of alteration. These mineral grains show partly still the characteristics of biotite, partly already those of chlorite. Accordingly, their alteration has not yet been completed.

The presence of a very simple mineral composition consisting of just a few minerals is shown by *Fig. 8*. The light-coloured minerals in the diagram are chlorites, the dark ones are predominantly chloritized biotites.

The source of this horizon seems to have been for the most part a magmatic area, though a redeposition is highly probable to have taken place. The composition shows many features akin to those of the Upper Pannonian formations. For instance, a common characteristic is the low number of minerals and the high quantity of chlorite. The difference between the two consists mainly in that the Upper Pannonian sediments are much less poorer in chloritized biotite.

3 C. Between 0,0 and 122 m the third Pleistocene heavy mineral horizon can be found. This horizon is more diversified in composition than all the preceding ones, differring very markedly from the underlying sequence *(Fig. 9, 10)*. This is indicated by the 12 minerals and groups of minerals shown in *Fig. 2*. as well.

The alluvium of the contemporary rivers of the Great Hungarian Plain are well known from earlier investigations. In the Great Hungarian Plain the composition of the sediments of the rivers is well differentiated from the composition of the foot-wall [B. MOLNÁR, 1964].

The difference in the heavy mineral composition between the alluvium of the present-day rivers and their foot-wall is indicated by a distinct boundary occurring at different depth, but available everywhere. This boundary appears everywhere, so at Jászladány as well, below, though close to, the *Viviparus böckhi* Horizon distinguished by M. KRETZOI and E. KROLOPP [1972]. A comparison of the composition of the uppermost mineral horizon of Pleistocene age at Jászladány with the alluvium of the present-day rivers allows one to conclude that the Jászladány horizon was deposited by the Zagyva river [B. MOLNÁR, 1964].

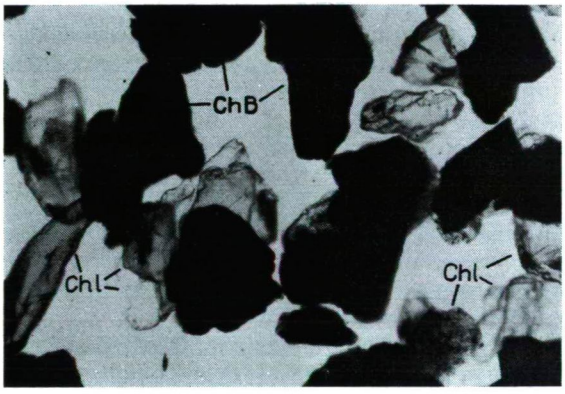

Fig. 8. Heavy minerals of the Pleistocene sands of Horizon *3B* from the 178, 7 to 178, 8 m interval of the Jászladány drilling (For explanation, see *Fig. 3*)

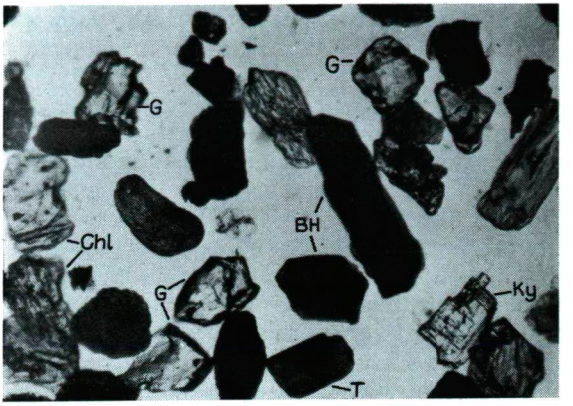

Fig. 9. Heavy minerals of the Pleistocene sands of Horizon *3C* from the 122,6 to 122,7 m interval of the Jászladány drilling (For explanations, see *Fig. 3*)

This composition is also characterized by the lower hypersthene, augite and basaltic amphibole content of the sediment as compared to the alluvium of most of the tributaries of the Tisza river. However, the percentage of garnet, magnetite and limonite is higher in it.

This third Pleistocene horizon of diversified heavy mineral composition resembles to the Levantine sequenc which differs from it primarily by the higher quantity of rhombic pyroxene (bronzite).

Analyses of the light fraction

The changes in source area observed as a result of heavy mineral analyses are also reflected by the quantitative and qualitative changes of the light minerals. Therefore analyses of the light fraction have been examined and grouped according to the depth intervals of the five different horizons.

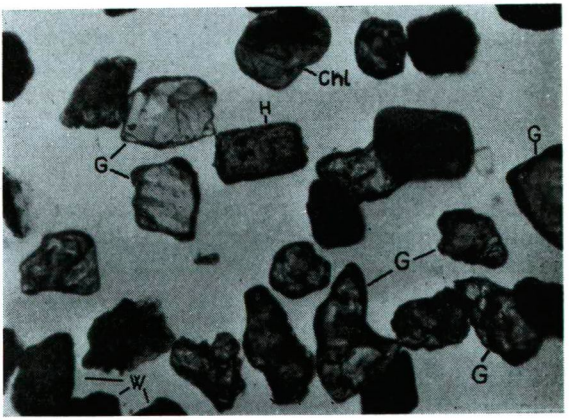

Fig. 10. Heavy minerals of the Pleistocene sands of Horizon *3C* from the 33,2 to 33,5 m interval of the Jászladány drilling (For explanation, see *Fig. 3*)

The samples were examined first macroscopically, with the aid of a stereo-binocular, then of a petrographic, microscope. The results can be summarized as follows:

The light fractions of the *Upper Pannonian* sands are light yellow in colour. In the samples the quartz grains are sharp-edged, splittery and limpid. Many quartz grains contain parallel arranged opaque inclusions: an indication of metamorphic sources. In a few samples they exhibit a very fine impregnation by pyrite. Potash feldspars are predominantly represented by orthoclases. Every sample contains a very high quantity of mica. Most of the micas are represented by muscovite, the smaller fraction by biotite. Chlorite grains are also frequent. Calcite-dolomite and light grey detrital carbonate grains are very great in number.

On the basis of the above, a considerable part of the material can be considered to have derived either from a slightly metamorphosed area or from a source rich in chlorite though previously metamorphic for the most part. The smaller fraction must have been introduced from a magmatic and carbonate rock source into the Jászság Basin.

The light fractions of the *Levantine* sands are light yellow in colour. The grains of the Levantine samples are somewhat less abundant in inclusions as compared to the Upper Pannonian sands. Inclusions, if any, are constituted by bulbs of liquids or gases. Needle-shaped crystals, however, may also occur as inclusions. All these features combined are indicative of a magmatic origin. Plagioclase grains showing polysynthetic twinning bands occur frequently. Potash feldspars are represented by plagioclases. Micas are poor in every sample.

Accordingly, the light fractions in the Levantine sequence differ in character from those of the Upper Pannonian and they indicate magmatic source to have been involved in the origin of the sediment.

The light fractions of the samples belonging to the Sequence *3 A of the Pleistocene* are light grey down to 317 m at the bottom. Above this level an alternation of light yellow and light grey sand layers can be observed. The grains in the light yellow sands are partly coated by finely distributed iron hydroxide. This coating is responsible for their yellow colour. The sand grains are sharp-edged, splittery and dull on their surface.

The quartz grains contain parallel arranged opaque inclusions, crystal inclusions being also frequent. Accordingly, the quartz grains partly suggest a metamorphic, partly a magmatic origin. Feldspars are represented predominantly by orthoclases. Among the plagioclases there are polysynthetic twins. The mica content is in all samples higher than was in the Levantine samples. The micas are represented predominantly by muscovite and biotite. Detrital carbonates and calcite-dolomite attain again considerable quantity. Most of the detrital carbonates are here, unlike the previously mentioned light grey ones, light yellow. In the yellow sands above the 317 m level the quantity of detrital carbonate and calcite-dolomite is somewhat lower than at the depths belonging to the Sequence *3 A* underneath.

Similarly to the heavy minerals, the character of the light minerals also indicates a source area of mixed genesis.

The light fractions of the samples belonging to the Sequence *3 B of the Pleistocene* are light yellow. The grains of the samples are partly coated. The quartz grains are sharp-edged, splittery and dull-surfaced. Many quartz grains contain opaque inclusions arranged in parallel. Like the former ones, the potash feldspars are represented by orthoclases. The mica content of the samples is mean. Detrital carbonate and calcite-dolomite are seldom present in them.

Accordingly, the source area of the sediment seems to have been of mixed genesis in this case, too.

Out of the samples belonging to *Pleistocene 3 C*, the sample deriving from 97 m is light yellow, the rest being light grey. The quartz grains are for the most part sharp-edged, splittery, but, unlike in the previous cases, rounded to well-rounded wind-blown sand grains occur frequently here. The quartz grains contain liquid, gas and crystal inclusions. The potash feldspars are predominantly orthoclses.

Muscovite, biotite and chlorite are poor in the samples, the same may be said of detrital carbonate and calcite-dolomite as well.

The sequence belonging to *3 C* had the same source as the present-day Zagyva river.

Next to do was to determine under stereomicroscope the *percentage distribution of quartz*, plagioclase and potash feldspar as found within the 0,1 to 0,2 mm fraction of the sand samples painted in slides by the Bailey—Stevens techniques (Table 1). Beside absolute percentage values the quartz-to-feldspar ratio and the plagioclase-to-potash feldspar ratio have also been calculated (*Fig. 11*, Table 2).

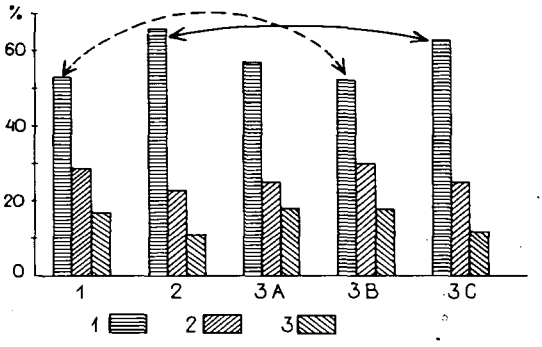

Fig. 11. Percentages of quartz and feldspar from the horizons of different heavy mineral composition of the Jászladány drilling profile

For explanations of *1*, *2*, *3A*, *3B*, and *3C*, see *Fig. 2.*

1. Quartz, *2.* Plagioclase, *3.* Potash feldspar. The arrows indicate the horizons of similar composition.

As evident from *Fig. 11*, quartz attains the highest value in the Levantine (66%) and the Pleistocene *3 C* sequence (63%). The lowest amount is found on its turn in the Upper Pannonian (53%), showing an affinity in terms of heavy mineral composition as well, and in the Pleistocene *3 B* horizon, second as counted from the base and very poor in heavy minerals (52%). In *Fig. 11*, the sequences showing affinity in terms of heavy mineral composition are connected by arrows.

According to *Fig. 11*, the affinity between the individual sequences is confirmed by both the subidentical percentage figures of quartz and the similar quantities of plagioclase and potash feldspar.

Alone the composition of the lowermost Pleistocene sequence (*3 A*) is different from all the others. It seems that the time of deposition of this very sequence was the period when the source area was the most diversified within the entire Pliocene

and Pleistocene of Jászladány. It is in this area that the transported sediments, wich both earlier and later derived only from one or the other of the areas, got mixed up. This is also suggested by the fact that the highest fluctuations in mineralogical composition of the entire sequence occur exactly here.

TABLE 2

Quartz-to-feldspar and plagioclase-to-potash feldspar ratios of sequences of different age in a borehole at Jászladány

Age and symbol of borehole		Quartz/feldspar ratio	Plagioclase/potash feldspar ratio
3 C	Pleistocene	1,70	2,08
3 B		1,08	1,67
3 A		1,33	1,39
2 Levantine		1,94	2,09
1 Upper Pannonian		1,14	1,77

The *average of the quartz-to-feldspar ratio*, grouped according to the five mineralogical horizons so far distinguished, are shown in Table 2. These values have been calculated from the data of Table 1. For instance, in the Upper Pannonian sequence the average of quartz as found in the seven samples examined is 53%. In the same sapmles the figure obtained for the two feldspar groups combined is 47%. The average of quartz has been divided by the average of the feldspars and so the value 1,14 characteristic of the Upper Pannonian was obtained. The ratios were calculated in the same way for the other sequences as well.

As evident from the results, the quartz-to-feldspar ratio markedly increases from the Upper Pannonian towards the Levantine, from 1,14 to 1,94; then, from there on, it shows again a marked decrease up to the Pleistocene *3 B* sequence (1,08). Finally, it attains the figure of 1,70 in Horizon *3 C*. It can be concluded from the results that in the Jászladány profile the least mature horizons are the Upper Pannonian and Pleistocene *3 B*, the most mature ones being the Levantine and Pleistocene *3 C*.

These data, however, are of relative value and are instructive only if related one to another. Namely, the high feldspar percentage of the sequence evidences that the absolute maturity of the sequence is still very low which is partly due to its relatively young geological age.

The similarity of the sequences showing up an affinity on the basis of the variation of the heavy mineral composition and of the quantity of quartz is confirmed by the similarity of the quartz-to-feldspar ratios.

The ratio of plagioclase to potash feldspar has also been calculated (Table 2). These values increase from the Upper Pannonian (1.77) towards the Levantine (2.09), to decrease then again up to Pleistocene *3 A* and attain, with 1,39, the lowest figure just there. This means that the difference between plagioclase and potash feldspar contents is the lowest in Horizon *3 A*.

Since potash feldspar too attains its maximum, beside *3 B*, here in *3 A*, this material or at least a considerable part of it derives from a somewhat more acid source. The same holds true of *3 B*.

The value of the plagioclase-to-potash feldspar ratio increases again from Pleistocene *3 A* to *3 C* (to 2,08).

EVALUATION OF CHANGES IN SOURCE AREA IN THE JÁSZSÁG BASIN

North of the Jászság Basin the Mátra Mountains still existing today and consisting predominantly of andesites were already present in Pliocene and Quaternary times. To the north of the mountains lay the Slovak Metalliferous Mountains including crystalline schists in their composition *(Fig. 1)*. To the east of the Slovak Metalliferous Mountains are the Gömörides containing considerable masses of carbonate rocks.

In the Pliocene and Quaternary this geological environment controlled the mineralogical and petrographic composition of the sediment that was being introduced into the Jászság Basin. In the Late Pannonian there was still a shallow-water lake in the territory of the Jászság Basin, but from the Late Pliocene (Levantine) on it was already characterized by terrestrial accumulation. As far as the conditions and characteristics of the accumulation taken place under such geological conditions are concerned, the following can be said.

The entire sequence examined is characterized, as compared to the composition of the other geological profiles of similar age of the Great Hungarian Plain, by the fact that the fluctuations in the percentages of the minerals occurring within single intervals of sediment of similar composition are here higher than elsewhere. This may be due to both the proximity of the basin margin and to rapid local changes of minor rivers.

The Jászladány profile is characterized by the fact that the biostratigraphic boundaries in it are at the same time boundaries of changes in mineralogical composition. So there is a marked change in source area at the Upper Pannonian-Levantine and the Levantine-Pleistocene boundaries. The Upper Pannonian and Levantine sequences cannot be further subdivided on the basis of the mineralogical composition. The Pleistocene sedimentary sequence includes further three horizons readily distinguishable from one another in terms of mineralogical composition.

The Upper Pannonian sequence shows a very monotonous composition. Its material derives either from a slightly metamorphosed source or from the redeposition of a chlorite-rich sediment. The influence of the near-by volcanic mountain is not reflected in it at all. This may be due to several causes. On the one hand, such of the volcanic area was then still covered by water so that little material could be transported from there into the Jászság Basin; on the other hand, the magmatic minerals could be lost from the sediment during weathering and diagenesis.

In Levantine time a paleogeographic change took place as compared to the earlier conditions. In the sequence there appear magmatic minerals along with metamorphic ones. Accordingly, the erosional area must have changed in the meantime. The removal of the sediment may also have been accelerated which prevented the minerals from any rapid weathering.

In the Levantine period the crystalline area of the Slovak Metalliferous Mountains contributed at an increasing rate to playing the role of sources, as evidenced by the relatively higher quantity of rutile *(Fig. 1)*.

From the Upper Pannonian Substage towards the Pleistocene the Pannonian shallow-water lake-sea was filled up, as shown for the Jászság Basin area, and in the Pleistocene it could witness only fluviatile sedimentation. It is the consequence of this paleogeographic change that the Pleistocene sedimentary sequence is not uniform in mineralogical composition, being split up into three parts. Accordingly, the source area must have thrice witnessed considerable paleogeographic changes. These were manifested on the basin margins by the appearance of rivers supplied by new source areas, in the Jászság Basin by the deposition of sediments of different mineralogical composition reflecting the corresponding change in the environment.

At the beginning of the Pleistocene (Horizon *3 A*) the rivers had partly still the ancient, partly by new, sources. Skirting the Mátra Mountains in the west and east, the rivers could have reached the Gömörides and the Bükk Mountains in the northwest and bring from those areas the considerable carbonate material of Horizon *3 A*. The afore-mentioned paleogeographic changes may have been responsible for the fact that Horizon *3 A* does not show a relationship with any other horizons.

The source area of Horizon *3 B* was partly simplified as compared to the former, as indicated most eloquently by the few heavy minerals present.

The present-day fluviatile drainage system, with the Zagyva river in its axis, was formed during the deposition of Horizon *C*.

The question that still remains to be answered in the following discussion concerns the difference of the present results from those of I. MIHÁLYI—LÁNYI and the new contribution that may be offered by the present study.

The most striking difference between the two authors' result consists in the percentages of the single minerals as related to one another. This is due, as indicated in introduction, to I. MIHÁLYI—LÁNYI's ignorance of the variation of grain composition in her investigations. In addition, she calculated the percentages of the abundance of the minerals by relying on one hundred determined grains only. Unlike her, the present author analyzed only the composition of small to fine sands and he determined three hundred heavy minerals grains from each sample. It was from these data that he has calculated the percentage of abundance of the single minerals (mineral variants).

The afore-mentioned circumstances are responsible for the further considerable changes as well. For instance, I. MIHÁLYI—LÁNYI supposes within just the Pleistocene interval nine changes to have taken place in the source area in accordance with the major fluctuations she found in mineralogical composition, whereas the present writer has presumed only three.

I. MIHÁLYI—LÁNYI believed much of the sediment below 199 m to have derived from the west, the Danube's drainage area. The mineralogical composition of the Danube's alluvium, however, is readily known from earlier investigations [B. MOLNÁR, 1964]. If these are compared with the present results, no evidence in favour of a western source effect can be found.

The results of the analyses of light minerals did well complement and confirm the analyses of heavy minerals. Similarly to the heavy mineral analyses, or parallel to them, the light mineral analyses also showed the analogies, or the dissimilarities, existing between the individual sedimentary sequences. The ratio of plagioclase to potash feldspar allowed the author to draw certain conclusions as to the petrochemical composition of the source area. Finally, information on the maturity of a sedimentary sequence has been supplied primarily by the light mineral analyses. These all were missing in I. MIHÁLYI—LÁNYI's results.

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MINERALOGICAL-PETROGRAPHICAL STUDIES ON MIDDLE TRIASSIC TUFFS OF THE TRANSDANUBIAN CENTRAL MOUNTAINS, HUNGARY

by
CSABA RAVASZ

During the researches of mineral raw material in the Transdanubian Central Mountains, we found some further occurrences of Middle Triassic pyroclastic material of more or less importance, after we had finished the manuscript of our previous publication [1970]. In the present paper we wish to give the petrographical description of these occurrences.

As can be seen from the geological profiles, these new occurrences can be brought into good agreement with the stratigraphical result of our investigations concerning the geological age of the tuff. All tuffs exposed belong to the Middle Triassic, to the lower part of the Ladinian. The places of sampling of tuffaceous material known up to now and the surface distribution of the Middle Triassic are shown in the geological sketch *(Fig. 1)*.

The borehole of the Bauxite Research Enterprise (No. Bsz1—5) is situated fifty kilometers north of the village Pécsely, in the northern foreground of the Bakony Mt. After Holocene, Pliocene, Lower Miocene, Upper Oligocene and Middle Eocene strata, the borehole crossed Lower Ladinian tuffaceous rocks. The underlying beds of the pyroclastic material investigated by us in detail (from 340 to 370 meter) consist of Middle Triassic dolomite, cherty dolomite, and cherty limestone. They are covered by cherty limestone. The thickness of the tuffaceous layers of the beds amounts to about 12 metres with thicker or thinner tuffaceous limestone and limestone.

The bauxite research borehole (No. Ma—50) near Magyaralmás crossed sandy, tuffaceous limestone overlying in round 10 m thickness Upper Anisian dolomite. The tuffaceous layers and the covering Diplopora dolomite are of Ladinian age *(Fig. 4)*.

Two shallow borings were, made near Vöröstó and Barnag, disclosed rather thin, tuffaceous limestone of light red and light brown color, deposited on Lower Anisian light red limestone containing many Ammonites. The overlying bed consists of red cherty limestone belonging to the upper part of the Ladinian. With this stratigraphical position, this tuff differs from the above mentioned formations and is the thinnest tuffaceous bed known up to the present *(Fig. 5)*.

The borehole of the Mecsek Ore Mines near Pécsely (No. P—8) crossed Lower Ladinian and Upper Anisian tuff sequences. The underlying layer of the 7 m thick tuff bed, containing phosphate bearing intercalations, is Megyehegy dolomite. Its overlying layer consists of light yellow, bedded, thick-laminated dolomitic limestone of about 40 m thickness, being at the same time the underlying rock

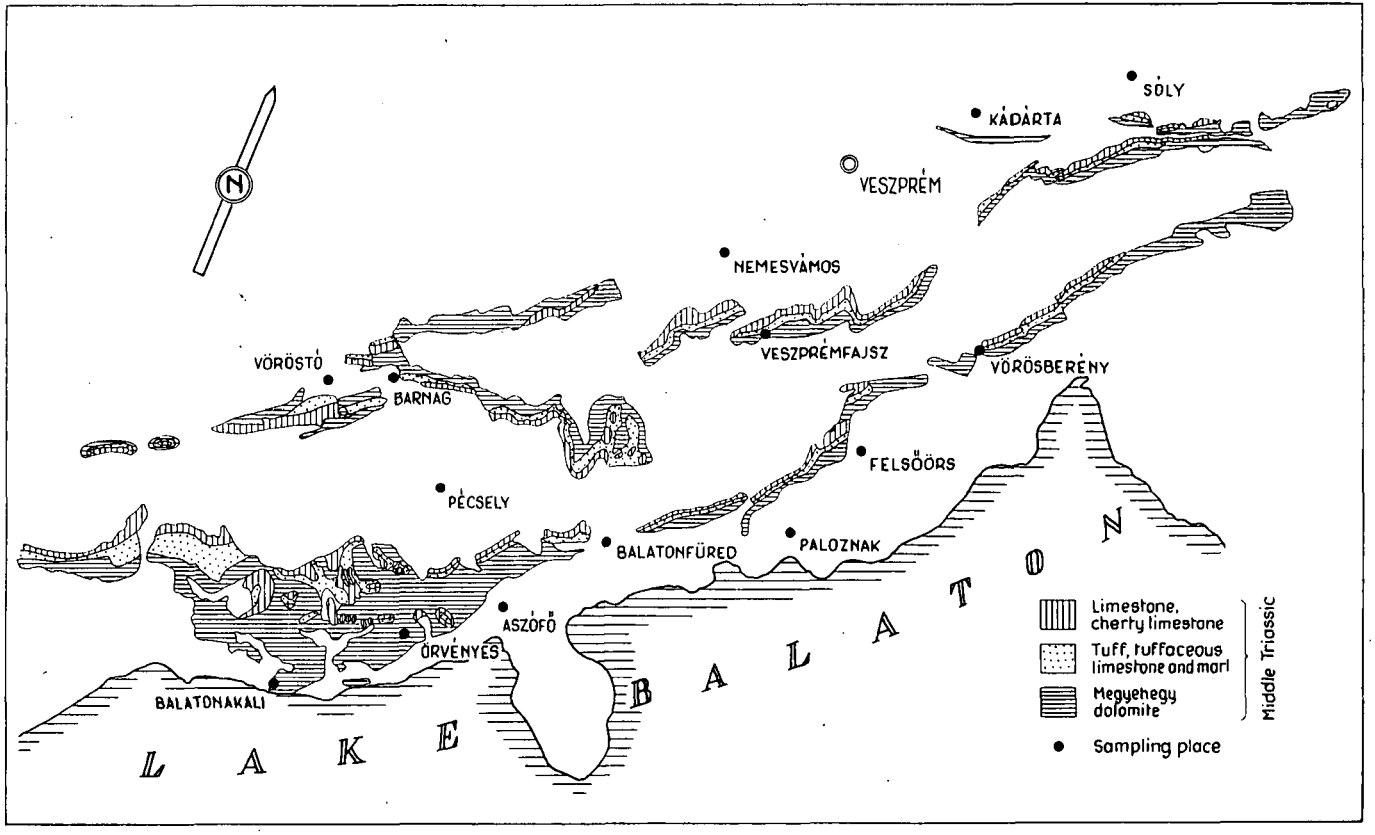

Fig. 1. Geological sketch of the distribution of the Middle Triassic formations in the area of Balaton Highland and Bakony Mountains.

for the upper tuff sequence *(Fig. 6)*. In the core sample of the same borehole, according to the investigations of the Hungarian Geological Institute, tuffite and trachyte tuff could be found above and below the layers studied by us at 322 m, 326 to 329 m, 387 to 390 m, and 466 m.. Together, the total thickness of the pyroclastic material in the profile can be estimated to about 20 meters *(Fig. 2)*.

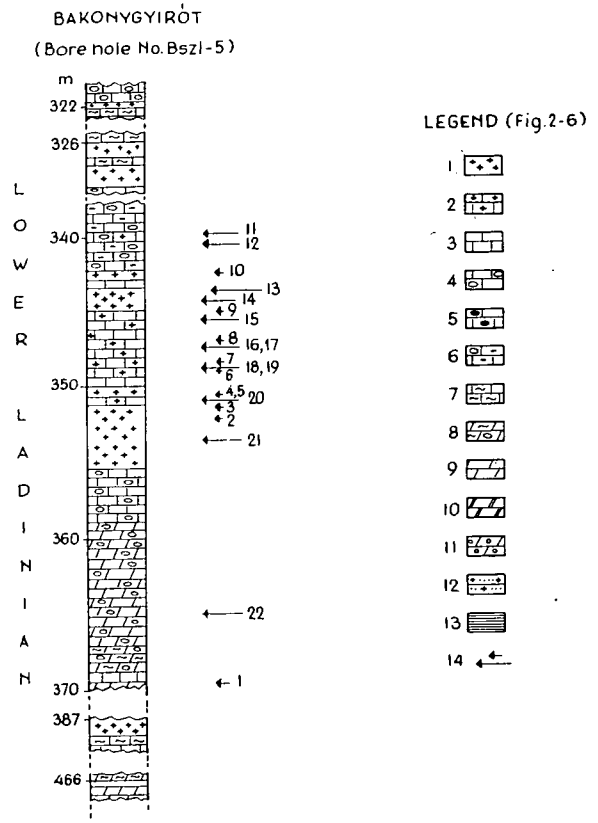

Fig. 2. Geological profile of Bakonygyirót borehole. No. Bszl-5. Legend: *1.* Tuff. — *2.* Tuffaceous limestone. — *3.* Limestone. — *4.* Cherty limestone. — *5.* Red, cherty limestone. — *6.* Cherty marl/clayey limestone. — *7.* Marly limestone. — *8.* Cherty, dolomitic marl. — *9.* Dolomite. — *10.* Megyehegy dolomite. — *11.* Diplopora dolomite. — *12.* Tuffaceous sandstone. — *13.* Bedded chert. — *14.* Number and place of sample.

On the Bocsár-Hill at Balatonfüred an exploratory trench made by the Mecsek Ore Mines exposed two tuff levels in the Lower Ladinian sequence of about 50 meter thickness. The deeper tuff layers are deposited on dark grey, Upper Anisian marly limestone, on a formation of so-called "reifling" type, characterized by Paraceratites trinodosus. The tuff layers of some centimeter alternate with bedded chert, and are separated from the upper tuff level by limestone containing cherty nodules. Also the latter sequence alternates with bedded chert, and is covered with Upper Ladinian limestone containing red cherty nodules. On the base of its fossil remains;

to the occurrence at Balatonfüred and of that at Veszprémfajsz, very similar to the latter in stratigraphical position are shown in *Fig. 3.*

During our earlier studies the potash-trachytic crystal tuff occurrence, considered as type-rock, was exposed by two exploratory trenches of the Mecsek Ore Mines. The Lower Ladinian tuffaceous materials deposited on the Megyehegy (?) dolomite: tuff, tuffaceous limestone, marl, clay, and sandstone frequently alternate with each other within some meters, and the thickness of pure tuff layers is limited to some centimeters *(Fig. 4).*

PETROGRAPHY

The quantity of the pyroclastic constituents of the tuffaceous rocks known from the core material of the Bakonygyirót research drilling is variable; even the composition of the ejected volcanic material is not uniform. Most frequently potash-trachytic crystal tuff and crystalloclastic limestone are found. Lithoclastic tuff occurs in minor quantities, vitroclastic constituents are to be considered as exceptional. It is characteristic, furthermore, that the thickness of each tuff layer does not exceed 40 cm; the structure of the tuff layers is laminated.

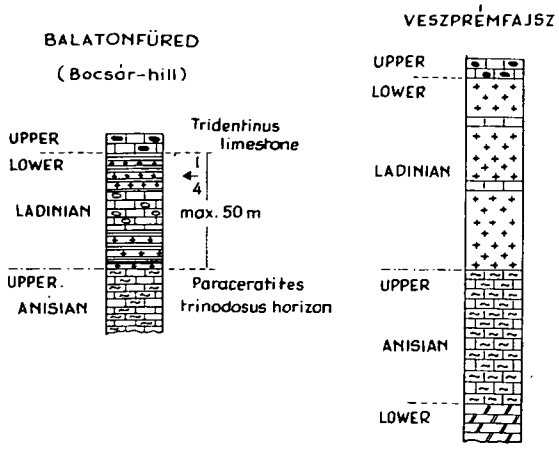

Fig. 3. Geological profile of tuffaceous beds at Bocsár Hill and Veszprémfajsz.

The typical crystal tuff in the borehole profile is macroscopically light green, grayish green, less frequently reddish brown or light red, of medium or low hardness, fine-grained, transected by calcite veinlets of dirty-white colour (samples No. 2, 3, 7).

Microscopically the bulk of the detrital material is sanidine. The greatest part of the crystals is hipidiomorphic, nearly idiomorphic or allotriomorphic fragments are seldom. Among the crystals of 200 to 300 μ, max. 500 μ dimensions the stubby habit is most frequent, elongated columnar forms are most seldom. Most of them are monocrystals, only few Carlsbad-twins are found. A minor proportion of the crystal fragments is fresh, pure or slightly clouded. Formation of sericite and illite along the cleavage planes and expansion of calcite and mosaic-like quartz is frequent. The last three minerals mostly form simultaneous pseudomorphs after sanidine.

The quantity of primary water-clear allotriomorph quartz of 50 to 150 μ grain size is insignificant. Similarly few more of less chloritized small biotite flakes of 50 to 120 μ in diameter are found. Apatite is accessory and oligoclase is sporadic (sample No. 3.).

Among the secondary minerals the anatase of stubby or elongated habit and 20 to 80 μ in length, found in small crystal aggregates, and forming pseudomorph

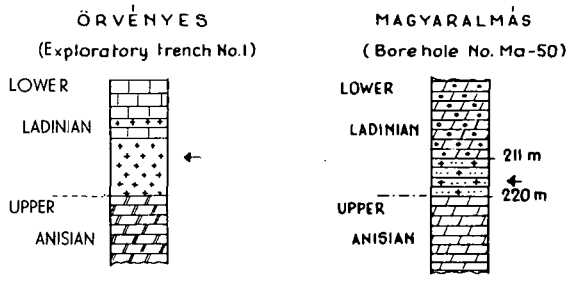

Fig. 4. Geological profile of tuffaceous layers at Örvényes exploratory trenches and Magyaralmás borehole.

after pyroxene is remarkable. The anatase is often pseudomorph with calcite, and forms the frame of the primary mineral, while calcite occupies the interior of the crystal. The place of opaque minerals is also replaced by secondary ores; limonite and leucoxene being formed from the original magnetite, ilmenite and pyrite (Plate III.). The lithoclastic material consists of recrystallized volcanic glass, feldspar microliths and limonitized opaque minerals.

The matrix of the rock is characterized by the illite-hydromuscovite netlace of threadlike structure in which patches of microcrystalline quartz, chalcedony and calcite crystal aggregates can be seen. Sporadically vaguely outlined parts of vesicular texture are observed (Plate I.).

The material of samples No. 5 and 6 is to be considered as a strongly silicificated (and recrystallized) variant, however, is of pyroclastic origin in the bulk.

Macroscopically the slightly cleaveable fine-grained tuff of light green or gray-green colour is mottled with coarser-grained, vivid green, light brick-red and brown intercalations. The matrix is less hard than the intercalations of various forms and colours.

Under the microscope the small quantity, small dimensions and the dominant role of microcrystalline quartz are characteristic. The material of the fragments of 50 to 100 μ in diamater on the average consists of sanidine, biotite and quartz. The feldspar in its lesser part is lath-like and idiomorphic, in its major part of max. 300 μ diamater hipidiomorphic, strongly argillaceous, or partly replaced by calcite and the latter by quartz. The quantity of primary quartz and of strongly altered biotite is small. The ore mineral of the rock is limonite in faint patches.

It is characteristic for the texture of the rock, that the illite, forming a not completely continuous network, encloses partly recrystallized volcanic glass, partly patches consisting of quartz crystals, 5 to 15 μ in diameter, originating from silica impregnation (Plate I.). The rock can be identified as decomposed, silicificated crystallo-vitroclastic tuff.

Chemical analyses of core samples of Bakonygyirót, borehole No. Bszl-5. Analysts: I. SOHA, L. JANKOVITS *Hungarian Geological Institute*

TABLE 1

Weight %	1	2	3	4	5	6	7	8	9	10
SiO_2	12,58	65,04	61,54	57,15	70,69	63,07	49,30	40,79	46,90	38,01
TiO_2	—	0,30	0,08	0,09	0,03	0,19	0,05	0,17	0,05	0,27
Al_2O_3	3,30	16,98	15,58	11,37	13,82	15,24	13,88	15,34	12,26	9,77
Fe_2O_3	0,35	0,68	0,75	0,38	0,55	2,29	0,71	1,11	0,51	1,85
FeO	0,45	0,81	0,94	0,63	0,72	0,81	0,85	0,90	0,76	1,39
MnO	0,05	0,03	0,03	0,02	0,03	0,03	0,03	0,03	0,03	0,06
MgO	17,81	0,42	2,24	1,12	1,41	3,18	3,64	4,20	3,08	7,02
CaO	26,35	1,95	3,51	11,91	0,88	1,57	11,71	14,25	14,84	17,20
Na_2O	0,05	0,06	0,08	0,09	0,20	0,14	0,06	0,06	0,08	0,12
K_2O	0,78	10,20	9,68	7,08	8,70	6,96	7,38	4,50	6,36	3,30
$+H_2O$	0,88	1,89	2,40	1,34	1,77	4,84	3,15	4,66	2,75	2,56
$-H_2O$	0,08	0,34	0,47	0,16	0,31	0,90	1,19	1,94	1,04	0,87
CO_2	38,01	0,77	2,59	8,92	0,56	0,42	8,41	11,84	11,36	17,44
P_2O_5	0,06	0,07	0,06	0,06	0,03	0,07	0,03	0,07	0,04	0,13
	100,75	99,54	99,95	100,32	99,70	99,71	100,39	99,86	100,06	99,99

For the tuffaceous limestone to be described in the following, the deformation (slumping) structure is generally characteristic. Namely, the pyroclastic material of these rocks is weak-laminated often found in nodules, grooved or cleaveing in lusterous shear planes, pinching or bulging out among limestone patches of ellipsoidal form or dissolved contours. In some samples the disturbed sedimentation, continued under changed conditions, can be traced in thin slides too. The subsequent processes of calcitization, dolomitization and silification are evident in most cases. This appears chiefly in the calcitization and replacement by quartz and chalcedony of the pyroclastic material, *i. e.* in the continuous decrease in quantity of the ejecta.

The embedding rock of the light green, slightly stratified, foliated crystalloclastic tuff intercalations is hard, compact, light red, brown mottled limestone with scattered pyrite (samples No. 4, 8, 17, 18).

Microscopically the majority of the pyroclastic material consists of allotriomorphic, more seldom hipidiomorphic sanidine crystal fragments. The diameter of the crystals is 50 to 150 μ, more rarely 200 to 350 μ, max. 1000 μ. The crystals are seldom fresh, they are replaced by illite, dolomite and calcite. The condition and quantity of biotite is variable. Its flakes, pleochroic or showing chloritization and ferrihydroxide precipitation, are of 200 to 250 μ in diameter. In sample No. 8, small quantities of water-clear, rounded and corroded quartz crystal can be identified. Among the secondary minerals the limonite, strongly staining its surroundings, is dominant; the quantity of the haematite, anatase and leucoxene is minimal. The fragments of fossils are filled by quartz; radiolaria skeletons are also found.

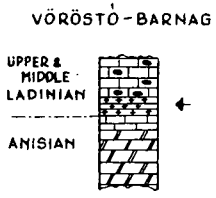

Fig. 5. Geological profile of tuff layers at Vöröstó and Barnag.

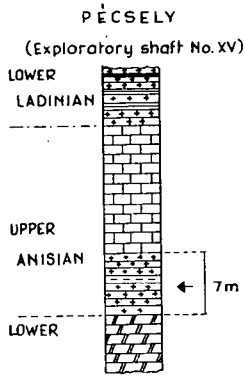

Fig. 6. Geological profile of Pécsely exploratory shaft.

The calcite, forming the bulk of the samples, is present in the form of allotriomorphic crystals of 20 to 30 μ diameter. As pseudomorph after feldspar or when filling up fissures, its diameter is 100 to 150 μ. A progressive state of silification can be observed on sample No. 18. The appearance of the mostly light brown chalcedony and of the minor quantities of water-clear microcrystalline quartz is variable. Both occur in separated patches of circular or irregular shape and as fragments of small spheres. In other cases, in the sections circular calcite fillings

are seen. Pellets of 1000 to 1200 μ in diameter and of circular or ovaloid section, coated with chalcedony, can be also found. The material of the pellets consists of a mixture of fine-grained calcite aggregates of mostly irregular shape and of impregnating chalcedony in the form of grains of 2 to 10 μ in diameter, recrystallized in different amounts. In these pellets, crystal fragments of potash-feldspar and biotite of 50 μ diameter on average are found. The margin of the pellet is a calcite corona coated by a thin chalcedony rim and surrounded again by a calcite margin merging into the limy matrix. The pellets containing no volcanogenic material have only a chalcedony coating. The tuff, falling into seawater, mixed with the lime mud of the bottom, and after diagenesis and silification consolidated as tuffaceous limestone. After braking up, calcarenite formed, which, during the repeated formation of tuffaceous limestone was built in as solid detritus into the matrix. The silica, enriched in the seawater by volcanic activity, may have been favourable for the proliferation of radiolaria. The siliceous solutions impregnated the shells of Mollusks and Brachiopoda and enhanced the formation of chert. The dolomitization occurred also during the rock consolidation and recrystallization. So the formation under investigation obtained its actual structure and composition, besides chemical precipitation, in addition by significant mechanical and less important biogenic effects.

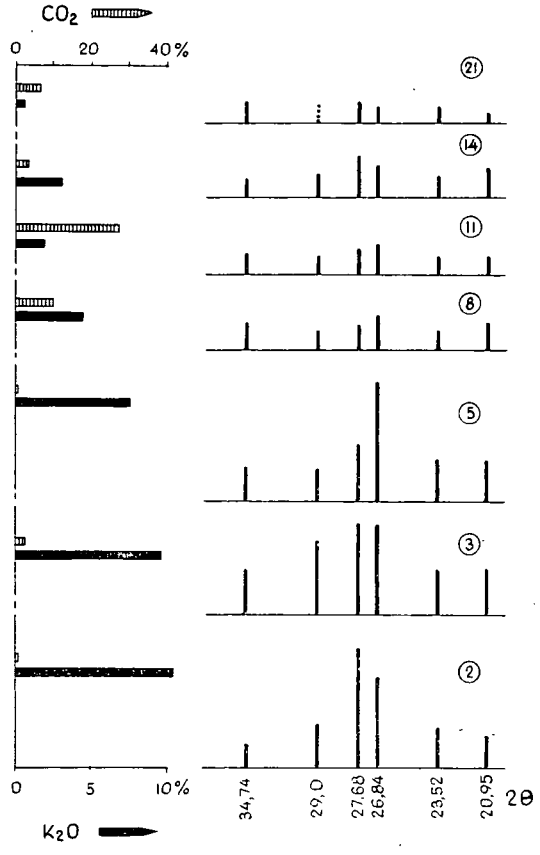

Fig. 7. Tuff — limestone ratio of the tuffaceous material of Bakonygyírót borehole (No. Bszl-5), characterized by the correlation of sanidine, K_2O, CO_2 content.

In two tuffaceous limestone samples (No. 9, 11), greater quantities of volcanic glass, associated with the crystalloclastic material, were found. Macroscopically the tuffaceous part can be distinguished from the greenish-gray limestone by its light green colour and its sheared structure.

Under the microscope, owing to clay-mineralization and calcareous replacement, only fragments of max. 100 μ diameter of the original sanidine crystal fragments of 250 to 300 μ diameter can be recognized. The small quantities of biotite are more or less altered, the primary quartz of minimal amount crenated, with embayed contours or of angular cross section. Accessory minerals are: apatite, zircon,

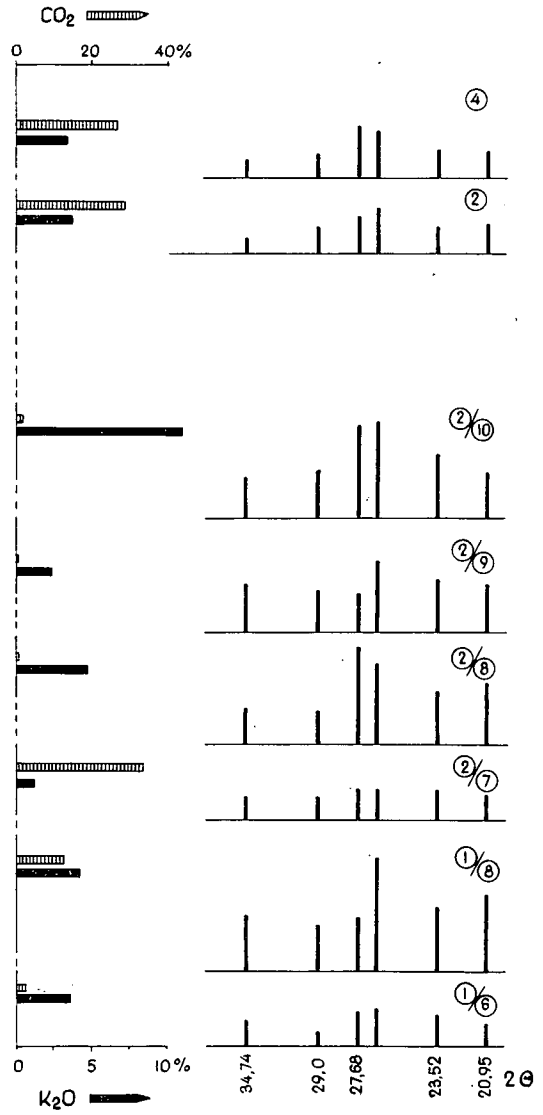

Fig. 8. Tuff — limestone ratio of the tuffaceous material of Barnag shallow boring (upper part),and Örvényes exploratory trenches (lower part), characterized by the correlation of sanidine, K_2O, CO_2 content.

anatase, limonite. Brown volcanic glass shards of pumiceous structure and somewhat higher index of refraction compared with canada balsam, chiefly recrystallized to chalcedony and quartz are found in somewhat greater quantities (Plate I.).

In the formation of pseudomorphs and even in the replacement of the material of the limestone, besides SiO_2, dolomite plays a comparatively very significant role.

A decrease in the amount of pyroclastic material is shown by two samples of silty limestone and one of fine-grained sandy limestone, taken from the tuff sequence. These rocks consist of allotriomorphic calcite crystals of 5 to 15 μ in diameter on the average, in which chert and comparatively great quantities of fossils can be determined. The expansion of the calcareous and siliceous material exceeds the grade of pseudomorph-formation and becomes dominant. The pyroclastic fragments consist of quartz, potash-feldspar, minimum quantities of plagioclase, chlorite, illite, zircon, epidote, apatite, pyrite, sphene; the contours of the trachyte fragments of the glassy matrix are dissolved. The average dimensions of the fragments are uniformly 10 to 30 μ, max. 100 μ (Plate III.).

Our attention was called to the rocks containing pyroclastic material, exposed in the Örvényes exploratory trench during our earlier investigations, when the tuff of the Upper Anisian sequence (Ágasmagas Hill, exploratory shaft No. 1) proved to be typical potash-trachytic crystal tuff. The material of the tuff intercalations in both trenches shows similarities, despite the differences in the embedding rock. The tuff in the upper level was lithoclastic, beneath it crystallo-lithoclastic, in the deeper level typical crystalloclastic potash-trachytic tuff was found.

TABLE 2

Trace element analyses of core samples of Bakonygyirót, borehole No. Bszl-5. Hungarian Geological Institute (ppm)

	B	Mn	Cu	Pb	Ga	V	Ti	Zn	Ni	Co	Sr	Cr	Ba	Li
1.	250	1000	40	4	4	25	600	<160	16	10	160	16	400	40
2.	160	160	60	6	25	25	6000	250	4	<6	160	4	400	40
3.	160	100	60	60	16	160	6000	160	16	16	160	40	400	40
4.	100	600	40	100	25	25	6000	<160	<4	<6	250	10	600	60
5.	100	160	25	<4	16	16	1600	<160	<4	<6	60	<2,5	400	60
6.	160	100	40	4	16	25	2500	250	4	<6	25	4	100	60
7.	100	400	25	10	16	16	2500	<160	4	<6	160	2,5	250	60
8.	100	600	25	16	16	25	4000	<160	10	<6	250	6	160	100
9.	100	600	25	25	16	40	2500	<160	<40	<6	250	4	400	60
10.	160	1600	100	4	16	60	4000	<160	40	16	250	60	400	60

Below the limit of detection are:

Be (250), As (600), Te (250), Hg (1000), Sb (160), Ge (25), W (100), Bi (25), Mo (10), Cd (60), Co (1600), In (4), Y (250), Sc (160), Nb (160), Tl (1), Sn (6), Ag (0,25)

The matrix of the macroscopically greenish-gray or light green lithoclastic tuff, often showing white or vivid green spots under the microscope proved to be clay-mineralized, calcitized and dolomitized. The glassy trachyte fragments and the small quantities of sanidine are not fresh. The matrix of the angular fragments, often subangular due to the calcareous replacement, is slightly devitrified rock glass, in which feldspar lathes of 50 to 100 μ in length, showing flow texture, are situated. The rather frequent light green patches of clay minerals containing calcite fillings in tiny vesicles or veinlets, are volcanogenic components, the original material of which cannot be traced back. Beside the Carlsbad-twinned sanidine some quartz and in isolated grains or aggregates and frames, leucoxene can be determined.

For the lower tuff levels, enrichment in sanidine crystal fragments and the decrease of the trachyte rock fragments is characteristic. These layers occur generally in light brown, reddish brown and light red limestone, cherty limestone, marl and clay. The material of light green or yellow-green colour, coarser grained than the embedding rock, is situated in thin streaks.

Microscopically the pure tuff, tuffaceous limestone, tuffaceous clay and their transitions can be well distinguished. The material of the crystal fragments is almost exclusively potash-feldspar. Its shape and dimensions are different, of 300 to 500 μ, some of 1200 μ diameter, the crystals are often idiomorphic, some specimens are slightly perthitic. Twin formation according to the Carlsbad twin law is frequent. Secondary minerals — in the order of their formation — are illite, sericite, glauconite, and, by replacement, chalcedony, dolomite and quartz. The presence of the original mafic silicates can be concluded only from the limonite, anatase, and glauconite observed in patches or frames. Accessory minerals are: apatite, perovskite. In some samples the enrichment of one of the above minerals (e. i. opaque constituents, glauconite) or the laminated structure is characteristic (Plate I, II.).

The material of the rock fragment is more or less clay-mineralized trachyte of similar dimensions and mineral composition as described above.

The rock varieties conisting of several sedimentary constituents contain fossil debris consisting of calcite and quartz material and pellets of calcareous material.

The thinner or thicker light green layers of the Bocsár Hill tuffaceous rocks can be well distinguished with naked eye from the gray, slaty bedded chert and the dirty-white radiolarian limestone layers bedded alternating with tuff.

In these sections, on the other hand, the presence of crystalline tuff components can be observed, though only in small quantities, in the bedded chert and limestone layers neighbouring the tuff, while the material of the layers considered as tuffs proves to be strongly silicified or calcitized; therefore, owing to the wide range of the transitions, it would be very difficult to draw sharp lithologic boundaries. The bedded chert contains calcareous (dolomite) and argillaceous (illite, chlorite) constituents, the cherty limestone significant quantities of quartz and chalcedony. I.e. the outcrop represents a sedimentary series, in which the volcanogenic material is demonstrated in the first line by the abundant SiO_2 rather than by the quantity of mineral fragments present. The interpretation of the microscopical picture was hampered by the darkening effect of opaque minerals of reddish-brown and black reflection, present in great quantities in different layers. The partly chloritized biotite of 60 to 70 μ diamater is comparatively frequent, quartz of 30 to 60 μ diameter is seldom, the alkali-amphibole of elongated columnar habit and 10 to 30 μ length is sporadic. The minimal quantities of sanidine, plagioclase, dolomite, illite can be demonstrated only by X-ray diffractograph. The radiolaria skeletons are frequent (Plate II.).

The material of the core sample from the Magyaralmás borehole is sandy limestone; among the detrital components, also material of pyroclastic origin can be found. Macroscopically the rock is coloured and appears as consisting of red-brown, dirty-white, and gray spots with light brown background.

Microscopically, built up allotriomorphic calcite crystals of 30 to 60 μ diamater, forming an almost equigranular texture, and great quantities of fine- and medium-grained sand, rounded in varying degrees can be seen in the limestone. Most of the detrital material is quartz of mixedly magmatic and metamorphic origin. The magmatic quartz is rounded in a lesser degree. Rock fragments, quartzite, muscovite bearing quartzite, recrystallized volcanic glass and pellets of limestone are found. The quantity of muscovite, potash-feldspar, and plagioclase is less than that of biotite; chlorite, clay-minerals, zircon, apatite is of minimal quantity. Few fossil debris of calcareous material are to be found.

In the light brown limestone of the Vörösberény road cutting, tuff intercalation of greenish brown colour is found. The pyroclastic material is represented chiefly by sanidine. The crystals of originally 500 to 600 μ diameter are practically pseudomorphs filled up by calcite, illite, and chalcedony, in which the feldspar has persisted only in small spots. Illite fragments containing round, pumiceous pores filled up with calcite, can also be found in this rock.

The Lower Ladinian compact limestone crossed by the Barnag shallow boring is characterized by vivid colour (yellow, light red, light green, reddish green), spotted, dendritic pattern and dissolved structure. In this hard rock strongly stained by haematite-limonite crystalloclastic-trachytic tuff of dirty-white or green colours occur in thin layers. The greater part of the crystal fragments consists sanidine of 300 to 500 μ in diameter, slightly clay-mineralized and partly replaced by calcite, dolomite and quartz. Water-clear, angular or resorbed and mostly ragged, weathered biotite of 150 to 200 μ in diamater is found in substantionally less quantity. Among the opaque minerals haematite occurs in great amounts, the anatase forming crystal aggregates is sporadic (Plate I, II.).

The macroscopically light brown rock covered by vivid green flakes, originating from Pécsely borehole, limestone with clay-mineralized pumice fragments. The material of the pumice is partly replaced by calcite and dolomite, partly clay-mineralized, chalcedonized. The original pores and holes of the fragments of 500 to 1000 μ diameter, are filled with brownish green illite and ivy green glauconite. The walls of the pores are lined with light brown chalcedony or ferrooxide-ferrihydroxide. Few crystal fragments are to be seen in the rock; a few zoned or albite-twinned fragments of water-clear oligoclase and a some scrabs of biotite. Chalcedony can be observed also in veins as a mineral replacing the calcareous material. As secondary cavity filling mineral or in thin veins also chlorite of apple-green can be found. The volcanogene pyroclastic material of the place of occurrence is calcalkali-type.

CONCLUSIONS

The composition of the material of the potash-trachytic tuff and tuffaceous materials investigated, supports our earlier opinion according to which the Middle Triassic pyroclastics, occurring in the Transdanubian Central Mountains, are to be considered as alkali (trachyte) magmatites instead of the composition thought earlier to be diabase. Furthermore, the recent investigations confirm our earlier observation that alkali character is exclusive in the Anisian and restricted to the

older formations, whereas in the upper part of the Ladinian a less amounts of pyroclastic material may occur, which gradually become of calcalkali-type.

Among the tuff varieties that of crystalloclastic composition is most frequent; this is often mixed with the trachytic-lithoclastic tuff. The vitroclastic variety occurs in comparatively small quantities. In the tuff sequences of the greater thickness, the production of volcanic material appears shifted from the crystalloclastic towards lithoclastic composition with the progress of time.

The tuff fell into seawater, and depending on its quantity, either thin layers consisting only of pyroclastics were formed, or more often it occurs as a detrital constituent in limestone, marl, dolomite host rock. The halmyrolitic weathering was extensive, in addition, the subsequent calcitization, silification, and dolomitization, leading to the decreasing quantity of the tuff were also important. Considering the quantity of sanidine crystal fragments and the carbonate content as the two most characteristic features of the tuff — limestone ratio, we wished to illustrate the changes in this ratio by plotting simultaneously the histograms of the percentual distribution of K_2O and CO_2 and the schematic diffractograms of the rock samples off our occurrences in *Figs. 7, 8.*

Examining the geological sections in their continuity, it can be easily seen, that the chert contant of the limy, clayey rocks, their frequent impregnation by silica, the presence of Radiolaria, in extreme cases the formation of bedded chert; i.e. the enrichment in SiO_2 is immediately connection with the quantity of the tuff fallen into the seawater.

The deformation structures observed and described, the pellett formation draw our attention to the mobility of the sedimentary basin. We consider these movements as due, in the first line, to tremblings connected with volcanic activity

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EXPLANATION OF PLATES

PLATE I

1. Sanidine and biotite in tuffaceous limestone. — Barnag, shallow boring No. Ba-2. — ‖ N, 30x.

2. Crystallo-lithoclastic tuff. — Örvényes, exploratory trench No. 1. — ‖ N, 50x.

3. Tuffaceous (crystalloclastic) limestone. — Bakonygyirót, borehole No. Bszl-5, sample No. 9. — + N, 30x.

4. Vitroclastic tuff. — Bakonygyirót, borehole No. Bszl-5, sample No. 5. — + N, 50x.

PLATE II

1. Illite in tuffaceous (lithoclastic) limestone. — Pécsely, borehole No. P—8. —‖ N, 30x.

2. Opaque minerals in bedded chert. — Bocsár Hill. — + N, 50x.

3. Glauconite and calcite pseudomorph after feldspar in tuffaceous limestone. — Örvényes, exploratory trench No. 1. — ‖ N, 50x.

4. Altered sanidine and biotite in tuffaceous (crystalloclastic) limestone. — Barnag, shallow boring No. Ba-2. — ‖ N, 50 .

PLATE III

1—2. Calcareous, clay-mineralized crystal-tuff. — Bakonygyirót, borehole No. Bszl-5, sample No. 7. — ‖ N (1), + N (2), 30x.

3. Silty limestone with fossil debris. — Bakonygyirót, borehole No. Bszl-5, sample No. 20. — ‖ N, 50x.

4. Cherty limestone with debris of radiolaria skeletons. — Bakonygyirót, borehole No. Bszl-5, sample No. 21. — ‖ N, 50x.


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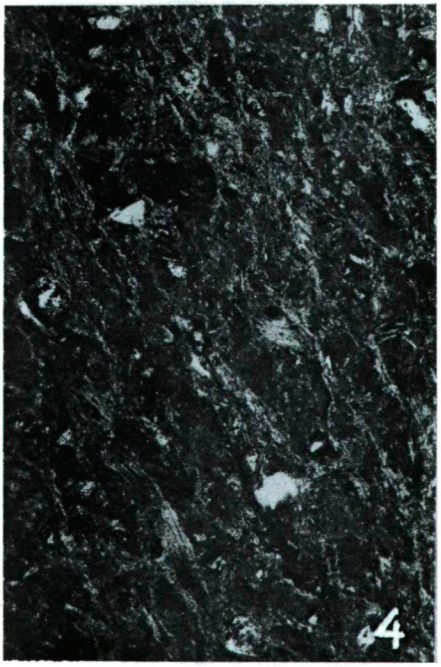
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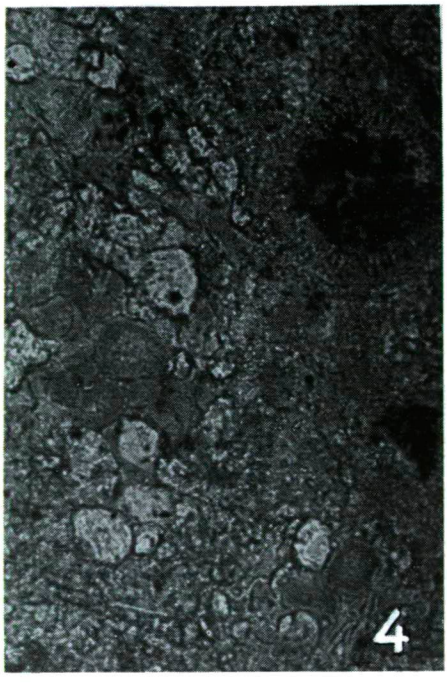
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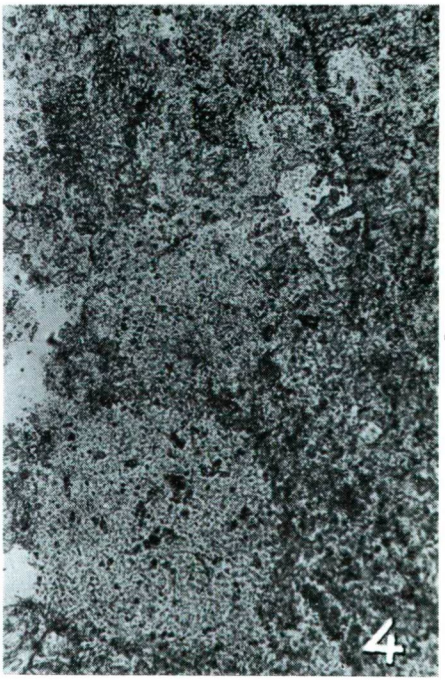
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GEOCHEMICAL ASPECTS OF FORMATION OF FERROMANGANESE ORES IN SHELF REGIONS OF RECENT SEAS

I. M. VARENTSOV

INTRODUCTION

Relatively large deposits of Mn and Fe-Mn ores which have been forming during the geological history within the existing continental frontiers are as a rule associated with the deposits of the shelf zones in the paleobasins. This is especially true of the past ore-bearing basins which have preserved fairly enough the initial relationships of the basic facies elements, these being Nikopol, Bolshoy—Tokmak deposits in the South-Ukraine Oligocene Basin, Chiatura and other deposits in Georgia [I. M. VARENTSOV, 1963, 1964; G. A. AVALIANI, 1967; I. M. VARENTSOV, E. S. BASILEVSKAYA *et al.*, 1967].

It is not infrequent that manganese and iron-manganese deposits are still discussed not from the standpoint of the conditions for ore accumulation proper, the obvious evidence for their association with the shelf zone being often the case, but from the standpoint of the nature of sources for ore-forming components. Numerous data have persisted into the recent time which are being used to substantiate either endogenous or, on the contrary, exogenous nature of ore components accumulating in the shelf zone of a basin. The study of the Chiatura Lower Oligocene deposit in Georgia, of the Varna Oligocene deposit in Bulgaria, of the Usin Lower Cambrian deposit in the Kuznetsk Alatau, the Upper Devonian Fe-Mn Deposits of the Atasui Region in the Central Kazakhstan and some others offers the examples of an attempted alternative solution for the problem of the nature of ore-forming components.

Although no recent basins displaying formation of manganese and iron-manganese ores can be directly compared with old ore-forming basins, the study of ore-formation processes is of some interest. Among other factors in such a study, the evaluation of those governing ore-formation stands most prominent: the features of localization of recent ore accumulation, sources for components, nature of solutions, geochemical features of environment, the mechanism governing the formation of ore substance accumulation. To put it another way, the study of formation of iron-manganese and manganese ores in the recent basins may prove to be one of the tools for obtaining knowledge on the past ore formation.

This paper aims at presenting the data of a comparative study of geochemical features involved in formation of iron-manganese ores with the conditions varying as wide as they do in such a basin as the Baltic Sea. The aim has stimulated the selection of the following study objects: the Gulf of Riga, the Gulf of Finland, the Central Baltic (the area of Gdansk and Klaipeda). For purposes of comparison, the data for other shelf basins are given too.

MATERIALS AND METHODS

The investigations are based on the data obtained from thorough work carried out in the ranges specially selected in the Gulf of Finland, the Gulf of Riga, and in the Central part of the Baltic Sea. The investigations were carried out within the joint programme sponsored by the Geological Institute, USSR Acad. Sc., and the Atlantic Division of the Institute for Oceanology in Kaliningrad (A. I. BLAZHCHISHIN). The stations were spaced from one another over the range's network at a distance of 0,5 to 4 km depending on the variations in sediments, the sea floor topography, the features of iron-manganese nodules and other characteristics.

The bottom sediments, the Mn-Fe nodules were sampled by dredging and coring. The water samples were taken by PVC bathometers. The operations performed aboard were as follows: water sample filtration with millipore filters (0,5 μ), pH measurements in the water and sediments with a ППМ—03 potentiometer, squeezing out interstitial waters. The samples were kept in the polyethylene vessels, the water was reduced by distilled acid for pH not to exceed 1,8.

The chemical analysis of iron-manganese nodules, crusts and silts has been performed at the Laboratory of the Geological Institute, USSR Acad. Sc., by the team of analysts M. I. STEPANETS, I. YU. LUBCHENKO, M. A. KANAKINA, E. V. SHURYGINA, headed by E. S. ZALMANZON. The methods applied rank among conventional ones. The content of Mn-Fe in the nodules as well as that of V, Cr, Cu, Ni, Co was estimated colorimetrically, that of Zn polarographically following the chromatographic separation. The elements present in the muds in smaller quantities were found by a quantitative spectral method.

The mineral content of Mn-Fe nodules was studied microscopically and by means of X-ray structural (G. V. SOKOLOVA of the USSR Academy of Sciences; Cr — anticathode, V — filter) and thermal analyses.

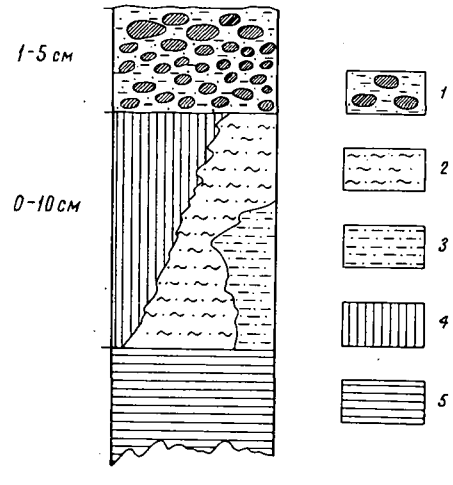

Fig. 1. Core of sediments from ore-bearing regions of the Gulf of Riga:
1 — Pisolitic nodules and their crust-shaped coalescences, of Mn and Fe hydroxides in the brownish watery mud;
2 — Greenish-gray, clayey silts;
3 — sand-clayey black muds frequently with H_2S;
4 — No sediments;
5 — Country deposits: glacial clays, yellow-grey

THE GULF OF RIGA

This region is essentially isolated from the main portion of the Baltic Sea, its sediment distribution being largely dependent upon specific features due to the discharge of the Daugava and, in part, the Lielupa [B. D. PUNTAS, V. G. ULST, V. B. EMES, 1968]. The Mn-Fe nodules found in the Gulf of Riga are mainly abundant over the relatively flat Saarema shallow water and over the slopes of the main trough of the 17—39 m depth. They occur in the upper (0—4 cm) layer of brown waterly mud which is frequently underlied by grey silts (0—6 cm), black oozes (0—7 cm) having no nodules *(Fig. 1)*.

The prevailing Mn-Fe nodules are those of spheroidal varieties, their crust-like accretions (2—30 mm on the average), the nucleus being in the form of terrigenous particles, compacted mud, etc. The nodules are mainly in the form amorphous iron hydroxide, hydrogoethite, goethite, birnessite, while manganese carbonate is considerably less abundant. Table 1 lists the chemical composition of the nodules.

The brown watery mud with Mn-Fe is characterized by pH 7,05; Eh+480 millivolts, the underlying dark-grey muds by pH 6,60—7,05; Eh+80—200 millivolts. See Table 2 for the chemical composition.

THE GULF OF FINLAND

The Gulf of Finland can be considered as a marginal-part of the Baltic Sea whose exchange with the main water mass of the basin is rather limited. The main hydrochemical features and sediment distribution are essentially dependent upon the discharge from the surrounding land; first of all upon that of the Neva, Narva and others, and upon an appreciable discharge from smaller channels of the Finland territory [B. WINTERHALTER, 1966].

The bottom of the Gulf of Finland is remarkable for its dissected topography. The sea hills, moderate elevations with relatively slow sedimentation have accumulated the nodules of manganese and iron hydroxides. The hollows, pockets of the sea relief accumulate black clay-silt muds, not infrequently with hydrogen sulphide (pH 7,60; Eh: −20 millivolts). In the northern and central parts of the Gulf of Finland, the comparatively small but well-pronounced elevations of the sea projections often display large (10×15) globular, compacted (up to 2—3 cm) nodules and crusts occurring over the surface of the basic light-grey morainic clays and sands.

A number of sections display a wide development of black pisolitic pieces (up to 2—5 cm) of a round botryoidal, frequently ellipsoidal shape, with hummocky surface. The nuclei of such nodules often have gravelly terrigenous particles and wood debris. Such nodules fill up (80—85%) the brownish-grey watery mud thick up to 5 cm. Below is black silt (7—10 cm thick) with plentiful fine vegetable remains and scarce nodules decreasing in quantity downwards.

The country grey morainic clays underlie black silts.

Occurring within the Gulf of Finland are also coin-shaped, disk-shaped varieties of nodules, coatings of pebbles, fragments of iron-manganese hydroxides.

The nodules and crusts occur mainly as goethite, hydrogoethite, amorphous iron hydroxides, birnessite, todorokite, with infrequently admixed amounts of manganocalcite. The chemical composition of nodules will be found in Table 1, that of muds in Table 2.

THE AREA OF GDANSK AND KLAIPEDA

This area can be considered the southern part of the Central Baltic which is a relatively open area of the basin with no pronounced localized source of sediments. Mn-Fe nodules, crusts occur mainly over the slopes of the plateau of the Gdansk—Gotland Rise, 60—104 m deep. They are associated with gravelly sands, sandy silts from 0 to 7 cm thick. As a rule the nodules, crusts, are found over the surface of these sediments or immediately on eroded rocks of country substratum represented by recent glacial clays, morainic loams *(Fig. 2)*. The depressions, pockets of the sea relief accumulate greenish-grey black muds, silts of up to 1,0 m thick [I. M. VARENTSOV, A. I. BLAZHCHISHIN, 1970].

The nodules, crusts occur as Mn-Fe hydroxides building up over the surface of altered clays, pebbles, terrigenous grains. Widely spread are crust-like formations over altered clays, coin-shaped, disk-shaped, less often pisolitic, buck-shot nodules, their aggregate, coallescences. They are represented by hydrohematite, hematite, amorphous iron hydroxides, todorokite, birnessite, rather seldom with manganocalcite. The chemical compositions of nodules, crusts are to be found in Table 1.

Dark-green, dark-grey muds filling in the depressions of substrata and black muds of the Gdansk and Gotland troughs vary rather moderately with respect to their compositions, although their Eh vary in a wide range (from −25 to +430 millivolts) with pH 6,70—7,70 (Table 2).

In spite of rather shallow depths, the bottom waters of this Baltic area display appreciably higher concentrations of Mn, Fe, Co, Ni, Zn, Pb (Table 3).*

The comparison between total concentration in the bottom water and the content of these elements in the water filtrated through the millipore filter of 0,5 μ pores allows a conclusion that a considerable part of these metals is found in the form which should be considered as dissolved.

DISCUSSION

The formations of iron-manganese nodules in the Gulf of Riga and the Gulf of Finland, and the Gdansk-Klaipeda area of the Baltic vary considerably, their major distinctions being as follows.

Mode of occurrence. The Mn-Fe nodules found in the Gulf of Riga and often those found in the Gulf of Finland are mostly present in the brownish watery mud (up to 5 cm) which spreads over rather thin (up to 7—10 cm) dark-grey silts, black muds with hydrogen sulphide. In most cases the brownish watery mud contains appreciable amounts of Mn-Fe nodules, up to 80% of the volume *(Fig. 1)*.

The nodules found in the Gdansk-Klaipeda areas occur as a rule over coarse clastic sediments, not infrequently upon the eroded surface of the main rock represented by glacial clays *(Fig. 2)*.

*) The analyses have been carried out by S. I. NEIMAN and D. L. ZALEV using Techtron AA-4 atomic absorber made by Varian Co. (at the Department for Analytical Chemistry of Moscow University). For this kind of water the limit of the method's sensitivity for the elements have been found in the following range (in μg/l), the figures in brackets show variation coefficients (in%): Mn 0,2 (22); Fe 1,5 (3,3), Co 0,6 (3,6), Ni 0,6 (2,8); Zn 0,4 (2,5); Pb 2,6 (5,0), Cu 0,5 (4,8).

Chemical Composition of iron-manganese nodules, crusts of the Gulf of Riga, the Gulf of Finland, and the Gdansk-Klaipeda areas in the Baltic

TABLE 1

Components	Gulf of Finland			Gulf of Riga			Gdansk-Klaipeda area			Black Sea (average)	Atlantic Ocean (average)	Pacific Ocean (average)
	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average			
1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	14.59	27.36	19.60	16.99	34.21	23.35	13.27	60.92	33.67	—	—	—
TiO_2	0.35	0.59	0.47	0.33	0.60	0,49	0.34	0.72	0.51	—	—	—
Al_2O_3	1.65	5.03	3.43	1.15	6.96	3.57	0.37	7.08	3.68	—	—	—
Fe_2O_3	14.65	40.03	28.02	17.95	52.30	32.41	16.29	35.15	26.17	—	—	—
FeO	0	0.55	0.10	0	0.64	0.12	0	0.71	0.19	—	—	—
CaO	1,85	2.92	2.38	1.25	2.84	1.90	1.21	1.84	1.50	—	—	—
MgO	0,11	0.71	0.35	0	1.10	0.71	0.88	1.43	1.07	—	—	—
MnO	1.63	5.15	3.29	0.40	7.60	2.84	0.13	6.05	1.98	—	—	—
MnO_2	2.93	28.06	17.06	1.04	24.01	11.90	1.38	21.33	11.26	—	—	—
Na_2O	1.14	1.74	1.41	0.60	1.92	1.05	0.81	1.48	1.18	—	—	—
K_2O	1.27	2.10	1.72	1.11	2.44	1.75	1.22	2.60	1.98	—	—	—
P_2O_5	0.56	4.58	2.85	0.57	2.98	1.59	1.13	3.78	2.53	—	—	—
CO_2	1.74	3.42	2.73	0.54	3.39	2.39	0.36	1.86	0.93	—	—	—
C_{org}	0.64	3.22	1.29	0.43	1.93	1.06	0.23	0.91	0.56	0.60	—	—
Fe_{total}	10.30	28.43	19.68	12.55	36.66	22.76	11,88	25.58	18.45	26.27	15.50	14.00
Fe^{2+}	0	0.43	0.08	0	0.50	0.10	0	0.55	0.15	—	—	—
Fe^{3+}	10.25	28.00	19.60	12.55	36.58	22.67	11.39	24.58	18.30			
Mn_{total}	7.06	21.72	13.32	0.97	20.69	9.70	0.97	15.88	8.65	6.90	13.55	24.20
Mn^{2+}	1.26	3.99	2.54	0.31	5.88	2.21	0.10	4.68	1.53	—	—	—
Mn^{4+}	1.85	17.73	10.78	0.66	15.17	7.52	0.87	13.48	7.11	—	—	—
Mn/Fe	0.685	0.764	0.677	0.077	0.564	0.426	0.082	0.646	0.468	0.26	0.87	1.73
P	0.24	2.00	1.24	0.25	1.30	0.70	0.49	1.65	1.02	—	—	—
Cr	12	28	17	12	36	23	14	43	30	—	—	10
V	34	90	68	32	134	98	123	157	134	—	—	540
Cu	3	20	9	1	65	17	9	100	42	40	1600	5300
Ni	5	106	35	3	150	47	40	250	148	280	3300	9900
Co	70	130	96	10	120	64	60	130	91	60	2400	3500
Zn	63	239	113	44	257	135	66	204	137	—	—	470
Pb	5	16	9	7	55	24	10	19	15	—	1200	900
Number of samples	—	—	9	—	—	19	—	—	7	—	—	—

NOTE. Content of main components is shown in weight %, that of minor constituents in n. 10^{-4}%

11. acc. to V. R. SEVASTYANOV, I. I. VOLKOV, [1966]. 12. acc. to F. T. MANHEIM [1965]. 13. acc. to J. MERO [1965].

*Content of Mn, Fe, P, V, Cr, Ni, Co, Cu, Pb, Mo, Ga, Ge in muds of the Gulf of Finland, the Gulf of Riga and the Gdansk-Klaipeda area of the Baltic**

TABLE 2

Components	Content**					
	Brownish watery muds	Black muds				Dark-green muds
	Gulf of Finland	Gulf of Riga	Gulf of Finland	Gulf of Riga	Gdansk-Klaipeda area	Gdansk—Klaipeda area
Fe_{total}	4.37—6.51 (5.25)	2.59—5.18 (3.78)	2.07—4.66 (3.74)	2.66	2.55—5.51 (4.39)	3.40—4.43 (3.93)
Mn_{total}	0.06—0 93 (0.37)	0.04—0.17 (0.10)	0.07—0.13 (0.10)	0.14	0.01—0.04 (0.03)	0.02—0.05 (0.04)
P	0.12—0.40 (0.24)	0.06—0.12 (0.09)	0.05—0.09 (0.07)	0.06	0.04—0.11 (0.07)	0.04—0.08 (0.06)
V	65—87 (76)	38—68 (59)	29—65 (51)	49	51—86 (68)	57—72 (68)
Cr	56—92 (71)	25—68 (48)	22—49 (39)	39	40—57 (50)	47—63 (54)
Ni	22—32 (27)	7—25 (17)	10—28 (21)	17	20—34 (26)	22—27 (24)
Co	12—20 (15)	6—11 (9)	7—19 (14)	7	9—11 (10)	8—13 (10)
Cu	48—66 (58)	10—29 (19)	13—32 (20)	21	3—26 (22)	25—35 (30)
Pb	66—93 (81)	18—39 (35)	16—58 (35)	30	32—99 (77)	40—78 (60)
Ge	1.9 —2.9 (2.10)	1.1 —2.2 (1.7)	1.1—16 (10.4)	1,6	15—20 (18)	1.2 —17.0 (10.4)
Mo	1.0 —108 (40)	1.0 —2.3 (1.4)	2.1—69 (52.4)	1.7	21—69 (35)	2.3 —46.0 (23.1)
Ga	23—28 (25)	9—26 (18)	12—21 (17.3)	16	17—32 (28)	22—24 (23)
Number of samples	3	6	3	1	5	5

* The figures in brackets show the average values.

** The main elements are given in weight percent; the minor ones in $n \cdot 10^{-4}$%.

Content of Mn, Fe, Co, Ni, Zn, Pb, Cu in sea water of the Gdansk-Klaipeda area of the Baltic, Station 1762 (depth 103 m)

TABLE 3

Nos	Depth (m)	Brief description	pH	Eh	Concentration (μg/l)						
					Mn	Fe	Co	Ni	Zn	Pb	Cu
1	0.0	Natural	8.20	+560	0.2	14.8	0.8	1.0	8.9	2.9	1.4
2	0.0	Filtrated through 0.5 μ filter			0.2	—	0.8	1.4	—	—	0.5
3	50.0	Filtrated through 0.5 μ filter	7.85	+560	0.3	19.1	1.25	2.0	41.5	3.9	2.80
4	75.0	Natural	7.10	+560	0.2	36.1	1.20	1.5	14.5	3.2	0.5
5	75.0	Filtrated through 0.5 μ filter			—	22.7	1.4	—	—	2.0	—
6		Bottom, filtrated through 0.5 μ filter	7.05	+490	4.1	28.9	1.0	1.7	37.7	8.6	0.6

Sources of ore-forming components. The sediments of the Gulf of Finland are supplied mainly by the Neva, Narva, Luga and other rivers. Special mention sould be made of the discharge from the territory of Finland and the Karelian Isthmus which brings considerable amounts of dissolved heavy metals, mainly humates. It should be pointed out that the peculiarities in the distribution of the continental discharge within the Gulf of Finland essentially govern the main features of hydrochemistry and distribution of sediments.

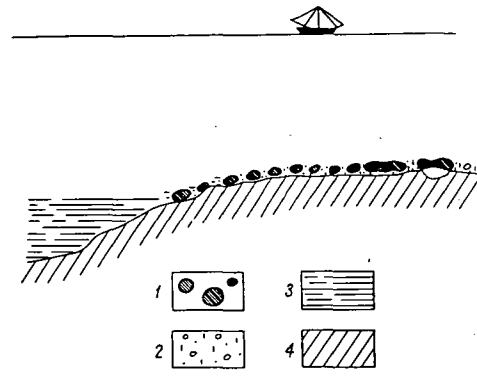

Fig. 2. Schematic representation of occurrence of Mn-Fe nodules, crusts at the bottom of the Gdansk-Klaipeda area of the Central Baltic:
1 — Mn, Fe nodules, crusts;
2 — Sandy-gravel;
3 — Black, dark-green clayey muds, frequently with H_2S;
4 — Country deposits: morainic clay, loams, etc.

The sediments of the Gulf of Riga are supplied mainly by the Daugava and, less so, by Lielupa and other rivers. The open part of the Baltic which is connected with the Gulf of Riga mainly through the Irben Strait influences its sedimentation but moderately.

The Gdansk-Klaipeda area can be considered an open part of the Baltic Sea which displays no clear-cut localized source for ore-forming components. In addition to the supplying of sediments from the mouths of the neighbouring rivers (the Vysla, the Neman) and the erosion of the country sea-floor rocks, the ore-forming elements are to a large extent supplied by currents whose mass contains Atlantic water incoming via the Danish Straits. There are some reasons suggesting that enrichment of the bottom waters with heavy metals can also be due, to a large extent, to the processes of their diffusion inflax from the sections of accumulation of dark, organic-rich muds neighbouring the concentration fields and from the stagnation zones of the area.

Morphology. The following varieties of nodules are widespread in the Gulf of Riga: pisolitic, buck-shot and their aggregate coalescences.

The Gulf of Finland contains spheroidal nodules and, occasionally, relatively large compacted varieties ($10\times15\times2$ cm), there are also disk- and coin-shaped nodules as well as fragments coated with Mn and Fe hydroxides.

The Gdansk-Klaipeda area is known for its comparatively widespread crusts and coatings ranging from pigmentation of boulder-and-pebble fragments with Mn and Fe

ydroxides to disk- and coin-shaped nodules. There are also rather numerous crust-like formations, mainly Fe hydroxides developing over the altered clays of he basic substratum. The spheroidal nodules, as a whole, are rather scarce in the dansk-Klaipeda area.

Mineral and chemical composition. While the mineral composition of Mn and e nodules, crusts, of the territories under study varies but slightly, their chemical composition testifies strongly to the particular conditions of their formation. Among ther factors these include the influence of the Atlantic waters (in the case of the dansk-Klaipeda area) and the effects due to the continental discharge in the bays hich brings fresh water.

One can, obviously, consider that, of the territories investigated, the most ronounced sea condition is found in the Gdansk-Klaipeda area while it is relatively oderate in the Gulf of Finland which is appreciably influenced by the river discharge. This can be illustrated by a relative comparison between the average content of nodule components over the three territories: the Gdansk-Klaipeda, he Gulf of Riga, the Gulf of Finland. The nodule components in the Gdansk-laipeda area is assumed to be a conventional unit. Then an increase in the relative content of CaO (1—1,27—1,59), Na_2O (1—0,89—1,19), CO_2 (1—2,57—2,94), $_{org}$ (1—1,89—2,30) testifies to the increasing effect of the river discharge upon he conditions of nodule formation. Conversely, the same order of a decrease in he relative content: MgO (1—0,64—0,33), K_2O (1—0,88—0,87), Cr (1—0,77—0,57), V (1—0,73—0,51), Cu (1—0,41—0,21), Ni (1—0,32—0,24), Zn (1—0,98—0,82) can e taken to account for a decrease in factors typical of the sea condition.

FORMATION OF Mn—Fe NODULES

The opinion on the process of formation of Mn-Fe nodules, the crusts in the dansk-Klaipeda area is based upon quite obvious and simple observations of their occurrence, structure, composition and the results obtained from the experi-ents by a number of authors [J. MORGAN, W. STUMM, 1965; G. MICHARD, 1969], s well as by our work on simulation of such phenomena. The data obtained allow judgement to the effect that Mn-Fe hydroxide nodules form due to selective chemisorption accumulation of transition elements followed by autocatalytic oxi-ation when active surfaces interact with bottom waters. Such surfaces can, to a ertain extent, be found in the altered terrigenous particles which have been leach-ed-out, in the fragments of the country glacial clays which often make up a nodule core or a base of crusts. When Mn and Fe hydroxides forming on such surfaces interact, during subsequent cycles, with bottom water, they show up as even more active sorbents as compared with the nucleus substance, the base. In other words, the products of such interaction promote the subsequent cycles of the process which leads to its autocatalytic nature. Each cycle of such a process includes several stages: the early stages cover a highly-selective ion exchange, molecular sorption ollowed by catalytic oxidation, formation of hydroxides, while the relatively more recent stages seem to include dehydration, transformation of the formed hydroxides. Apart from the formation of the hydroxide phases of Mn, Fe and other transitional metals, there also form authigenic silicates, rather complex spinel-like compounds.

This process can be contributed to by relatively slow terrigenous sedimentation or no sedimentation at all (the terrigenous clayey particles block the active surfaces), by bottom currents which carry considerable masses of component containing

solutions over the active surfaces, by positive values of Eh. Such a process can take place in a wide range of the concentrations of the accumulated components: 10^{-2}—10^4 µg/l.

The Mn-Fe nodules found in the Gulf of Riga and, to a large extent, in the Gulf of Finland, as shown above, differ from the nodules found in the open sea as to their conditions of occurrence, morphology, structure and composition.

For Mn-Fe nodules found in the Gulf of Riga and those in a number of areas of the Gulf of Finland their occurring conditions are of importance. Let us consider them using a respresentative example of the Gulf of Riga. In many cases, though far from all of them, the nodule-containing brownish watery mud (3—5 cm) is underlain by the grey silts (up to 5—7 cm) with black clayey organic-rich muds having H_2S usually being below it *(Fig. 1)*. In interstitial waters of such black, grey clayey silts there are, according to T. I. GORSHKOVA [1970], relatively high concentrations of Mn (up to 8,46 mg/l) and Fe (up to 2,28 mg/l). A high gradient of concetration of Mn and Fe in interstitial and bottom water in the accumulation areas of these sediments suggests a question on the likely role of Mn and Fe diffusing upwards, from the relatively concentrated interstitial solutions into the layer of watery mud, containing the nodules of Mn, Fe hydroxydes.

To estimate a relative share of Mn and Fe diffusing upwards from the relatively reduced layers of the sediment in the total balance of these elements during formation of nodules, the calculations were made wherein the part of the factors favouring diagenetic processes was purposefully exaggerated. For detailed substantiation of such calculations, taken as a reference was a representative station No. 1788 in the Gulf of Riga (depth 22,0 m, lat. 58°00′2, N long 22°30′7 E), water-depth 0,0 m, pH 8,35; Eh +560 mV, depth 22,0 m, pH 7,20; Eh +560 millivolts. The water core of this station is represented as follows: 0—3 cm of brownish watery mud, containing up to 70% of spheroidal nodules (1—3 mm) of Mn, Fe hydroxides which frequently form accretions; 3—8 cm of greenish-grey mud, silty, having no hydroxide Mn-Fe nodules; 8—10 cm of black mud, silty-clayey, organic-enriched, stinking of H_2S. Below are pale-grey, thin, glacial clays.

The calculations have been based on the following assumptions: the content of manganese-iron hydroxide nodules in the brownish watery mud — 10%, thickness of mud — 1 cm. The nodules contain Mn — 10%, Fe — 20%, the specific gravity of nodules — 2,5 g/cm³ (*i. e.* these characteristics are taken to be somewhat higher than actual ones). The thickness of grey silts is 10 cm, that of black clayey muds containing H_2S is also 10 cm. The humidity of the two types of muds is assumed to be 80%, the concentration of Mn in the solution of mud is 20 mg/l, that of Fe is 5 mg/l. It is admitted that all the quantities of Mn and Fe present in the solution diffuse entirely upwards to take part in the formation of nodules.

The calculations show that the quantities of Mn and Fe present in the solution of mud comprise but 1,28% of the quantity of Mn and 0,16% of Fe found in the nodules. Thus to provide the accumulating amounts of Mn and Fe in the hydroxide nodules according to the above assumptions and with a mere diffusion inflow o these components from the mud solutions of lower sediments, the thickness of the latter must have been 17 m for the case of Mn, and 125 m for Fe.

However, the rate of sedimentation within the areas of Mn-Fe nodule formation in the Gulf of Riga and the Gulf of Finland is relatively slow, not more than 20 cm of sedimentation column has accumulated since the recent glaciation (about 10 000 years).

Thus, the diffusion supply of Mn and Fe due to diagenetic phenomena in relatively reduced sediment layers in the Gulf of Riga and the Gulf of Finland is practically within one per cent of the Mn and Fe amounts accumulated in the nodules.

The estimations of the relative share of Mn in the total balance of supply of this element in the formation of oceanic abyssal nodules [M. L. BENDER, 1971] also testifies to a negligent role of the Mn diffusion influx from the lower layers of sediment.

The above data and estimations suggest that Mn-Fe nodules in the Gulf of Riga and the Gulf of Finland were formed due to the selective and chemosorptive mechanisms and that of autocatalytic interaction between the solution and the active surfaces. In the cases under consideration, the feature of Mn-Fe nodule formation is that, along with the solute-state metals, the gulf is supplied with their suspension-state varieties as humates, organic and mineral particles. These metal-containing suspensions decompose both in the water mass proper of the gulfs and in the upper horizons of the sediment where Mn and Fe came into the solution. This is testified to by their high concentrations in the interstitial waters of the brownish muds: Mn up to 18 mg/l, Fe up to 1,33 mg/l [T. J. GORSHKOVA, 1970].

BRIEF REVIEW OF GEOCHEMICAL ASPECTS OF FORMATION OF Mn—Fe NODULES, CRUSTS IN THE SHELF REGIONS OF SEAS

The works of F. T. MANHEIM [1965] and T. I. GORSHKOVA [1967] contain an extensive review of the conditions of formation of manganese-iron nodules in relatively shallow seas.

The nodules found in the shelf zone of the Black Sea, near the Crimean coast, south of Tarkhankut have been described by V. R. SEVASTYANOV and I. I. VOLKOV [1966], those in the Rumanian coast littoral near Constanța and Sulin (depth of 40 to 60 m) by LU. GEORGESCU and S. LUPAN [1971].

Comparison of the data obtained by these authors with the characteristics available for the nodules in the Gulf of Finland, the Gulf of Riga, the Gdansk-Klaipeda area of the Central Baltic goes to prove that they share some common features: the conditions of occurrence, localization, structure, mineral and chemical composition. For instance, the mean composition of Mn-Fe nodules in the Black Sea [V. R. SEVASTYANOV, I. I. VOLKOV, 1966] differs but slightly from that of Mn-Fe nodules in the Gdansk-Klaipeda area of the Central Baltic (Table 1). At the same time, the chemical composition of Mn-Fe nodules in the shelf basins differs markedly from that of the nodules in the Atlantic and the Pacific (Table 1). As stated above, with a decrease in the continental discharge, in particular in the river discharge, the relative content of Mg, K and especially of minor elements — V, Cu, Ni, Zn — increases appreciably. However, in one studies the changes in the chemical composition of Mn-Fe nodules in a succession reflecting a decrease in the continental discharge: the Gdansk-Klaipeda area of the Baltic — the Atlantic — the Pacific (Table 1), one cannot help noticing a marked growth of the Mn/Fe ratio and the contents of V, Cu, Ni, Co.

It was stated earlier [I. M. VARENTSOV, 1972], that the formation of Mn-Fe oxide ores in the existing basins can be considered to depend upon the reactive mechanism of the selective, chemosorptive interaction, along with autocatalytic oxidation, between the active surfaces and the component containing solutions. In the oceanic basins, such a mechanism of formation seems to be no less obvious

and possible than in the shelf waters. As to the differences in chemical composition of manganese-iron nodules in these basins, they can be accounted for proceeding from the study of the composition of interacting waters, sources (in particular of endogenic ones), the conditions of dissolved oxygen, pH, Eh, sedimentation rates, etc.

An analysis of paleogeographic conditions acting in formation of relatively large manganese and iron-manganese deposits within the existing continental boundaries strongly testifies to their formation in the shelf basins.

Though direct extrapolation would be unacceptable, the knowledge of the processes involved in formation of Mn-Fe ores in the shelf regions of modern seas can be made use of when studying ore formation in old basins.

CONCLUSIONS

1. The main factors have been considered which govern formation of Mn-Fe ores in the Gulf of Riga, the Gulf of Finland, the Gdansk-Klaipeda area of the Central Baltic. The formation of Mn-Fe ores takes place within the sites of weaker sedimentation, such as slopes, peaks of submarine elevations, localities of submarine erosion of the country bottom rocks, etc.

2. The chemical composition of the ores regularly changes following the looser connection with the open sea basin and stronger influence of the river discharge (the Gdansk-Klaipeda area — the Gulf of Riga — the Gulf of Finland). This succession displays a regular decrease in the content of Mg, K, Cr, V, Cu, Ni, Zn while the amounts of Ca, Na, CO_2, C_{org} rise.

3. The processes involved in formation of oxide ores can be considered to depend upon highly selective, chemosorptive accumulation of Mn and Fe and other transition metals with their autocatalytic oxidation while the active surfaces interact with the bottom waters.

4. The calculation of the diffusion inflow of Mn and Fe from the reduced muds when they underlie Mn and Fe nodules (the Gulf of Riga) shows that this is responsible for as little as 1—2% of Mn and Fe accumulated in nodules.

5. The study of ore formation in shelf regions of other seas allows a conclusion to be drawn that the ores forming in such conditions are rather similar in their composition but differ greatly from Fe-Mn nodules found in the open sea containing, as they do, an essentially poorer minor elements associations, and essentially smaller concentrations and values of Mn/Fe ratios.

6. Though direct extrapolations would be unacceptable, the knowledge of the processes involved in formation of Mn-Fe ores in shelf regions of modern seas can be made use of in studying ore formation in old basins.

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LETTERS OF THE COMMISSION ON MANGANESE (IAGOD)

PROGRESS REPORT ON RESEARCH IN MANGANESE ORE DEPOSITS OF ROMANIA (1971—1972)

RADU DIMITRESCU

In the last two years geological, mineralogical and geochemical investigation uf the Romanian manganese ores continued only for the East Carpathian metaoorphic deposits, the only ones with present commercial value.

For the recently identified Iacobeni kutnahorite, chemical, X-ray, DTA, optical and IR analyses are given by BĂLANC.

Carbonates (rhodochrosite-ponite), pyroxenes (rhodonite-pyroxmangite) and garnets (spessartine) from Şarul Dornei were analyzed by POPA. The same author has investigated statistical correlation between Mn, Fe and minor elements (Ni, Co, Cr, V, Mo, Cu, Zn, Pb) in the manganese ores of the deposit, volcanogenous — sedimentary premetamorphic origin being substantiated. Smaller ore deposits were also studied: Dadu Mt. (IDRICEANU *et al.*) is the northernmost deposit of the Bukovina and Borca (ZLATAROVA—MUREŞAN) is the southernmost one. Their geochemical characteristics were emphasized, mainly by graphical methods. Metamorphic manganese ores of the same type as in the Bukovina, were identified and described in the Maramureş by CIORNEI.

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